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HUMAN METABOLISM IN AN ENVIRONMENT OF HEATED AIR

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The effect of an environment of heated air upon the loss of heat is easy to understand, but the influence of such an environment upon heat production has been only superficially investigated. Many studies made under tropical conditions show, unfortunately, rather wide divergence in results, and knowledge with regard to the influence of a hot environment upon metabolism is much needed. At Bellevue Hospital a machine designed for delivering rather large volumes of highly desiccated, heated air over the nude body of a human subject placed in an air-tight bag enabled us to make observations with regard to the metabolism, pulse-rate, respiration-rate, and body and skin temperatures.

Three men and two women served as subjects. The three men were of normal build with pelidisi of 98, 99, and 96, respectively. The two women were fat, and the pelidisi of one was 118 and of the other 106 (see Table 1).

Table 1

Height, Weight and Pelidisi of Subjects

Subject	Height cm.	Nude Weight kg.	Pelidisi
Mr. D.	181	83.4	98
Mr. E.	170	70.0	99
Dr. D. B.	180	75.0	96
Mrs. F.	161	105.4	118
Miss G.	171	90.8	106

The metabolism was studied by means of a portable respiration apparatus with internal blower.[1] The body and skin temperatures were studied with a thermo-electric element.[2] The temperature of the air enter-

ing the bag was usually not far from 85°C., and the sojourn in the hot air was about one hour.

There was an excessive loss of perspiration, the body frequently being bathed with moisture. The loss in weight under these conditions varied from 220 to 660 grams per hour, being roughly proportional to the size of the individual. As the normal loss in weight of a nude human in room air is about 40 to 50 grams per hour, the heated air produced a loss from 5 to 13 times greater. Since the metabolism measurements showed but a small increase in the oxygen consumption, representing oxidation of body tissue, the increase in loss in weight is due almost exclusively to the increase in perspiration.

The hot air caused a marked increase in respiration-rate with one subject, but with two others it had no appreciable effect. The pulse-rate was definitely increased by the hot air.

The mouth temperature was taken before and after the sojourn in the hot air with only one subject. In this case the mouth temperature tended to increase as the sojourn in the air continued.

The air entering the chamber near the right foot was usually somewhat over 80°C. and at the point of exit near the left shoulder it was not far from 45°C. Thus the temperature of the air about the legs of the subject was much higher than his skin temperature, but the temperature of the air in close proximity to the skin around the upper part of the body was not much higher than that of the skin itself.

In the case of the three men it was found that the hot air had no appreciable effect upon the rectal temperature. With the rather stout woman having a pelidisi of 106 the vaginal temperature distinctly increased during the sojourn in the air, an increase of 1°C. in 70 minutes being noted.

The temperature gradient ordinarily existing between the vaginal or rectal temperature and the skin temperature completely disappeared as a result of the hot-air bath in the case of the woman subject with whom vaginal temperatures were obtained.

A fairly uniform skin temperature obtained over the whole body as a result of the hot-air bath. On the average this temperature was one or more degrees higher than the skin temperature under ordinary conditions. The rapid cooling effect of the vaporization of water lowered the skin temperature in the hot air so that at no time was it higher than the normal rectal temperature.

The gaseous metabolism could be studied only with the three men, with whom observations were made prior to (under normal·basal conditions) and during the sojourn in the hot-air environment. There was an increased oxygen consumption during the sojourn in the hot air, amounting to from 5 to 10 per cent after 1 to $1^1/_2$ hours in the hot environment.

While this investigation is by no means complete, it indicates the im-

portance to pure physiology of studying the influence of the environmental temperatures and humidities existing in the tropics upon normal heat production and heat loss.

(The details of this investigation will be reported in a forthcoming number of the *American Journal of Physiology*.)

[1] Benedict and Collins, *Boston Med. and Surg. Journ.*, **183**, 449 (1920).

[2] Benedict, Miles, and Johnson, *Proc. Nat. Acad. Sci.*, **5**, 218 (1919).

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*INVARIABLE OCCURRENCE OF MALE STERILITY WITH DIETARIES LACKING FAT SOLUBLE VITAMINE E**

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It has already been possible to show[1] that in the female, sterility may be produced by dietary regimes which nevertheless contain the known vitamines and are adequate for growth. We have reported the cure of such sterility by a variety of natural foods and by small doses of alcoholic and ethereal extracts of those foods. The evidence at hand is thus conclusively in favor of the existence of a new vitamine or food accessory to which the designation of fat soluble E^{1a} may be given.

When male rats from mothers on natural foods are weaned on the twenty-first day of life and then reared upon a basal or "pure" food ration, they are usually at first fertile but when from ninety to one hundred and fifty days of age (usually at the close of the fourth month) become sterile. In a large group we have encountered one or two instances of retention of this initial fertility for a period of seven months, but this is exceptional. The sterility which supervenes in animals held upon these rations, while variable in the exact time of its appearance, is invariable in its ultimate occurrence. At the present time, though many experiments are in progress, completed studies may be summarized as follows: A total of one hundred and eighty males (rats) have been maintained on such a basal diet or modification of it and submitted to repeated functional tests, several thousand "positive"[2] matings with females of proven fertility having been carefully followed. The distribution of animals with reference to the dietaries employed may be seen from the following table. The animals were invariably sterile.

We have studied fifteen "second and third generation" males. Their mothers had been reared on the basal ration, fertility having been induced by the administration of minute amounts of highly concentrated extracts

of vitamine E. The sons were now similarly reared. *Such males are sterile from the beginning of sexual maturity.*

EXISTENCE OF STERILITY IN MALE RATS, REARED AND HELD ON THE BASIC RATION OR MODIFICATIONS OF IT

DIET	NUMBER OF MALES BRED	NUMBER OF MALES STERILE
B.R. (Basic Ration)—Casein 18, Cornstarch 54, Lard 15, Milkfat 9, Salts 4, Yeast 0.4–0.6 gram daily	52	52
B.R. No. 60—Casein (extracted) 18, Cornstarch 54, Lard 22, Cod Liver Oil 2, Salts 4, various levels yeast (0.2 to 1.6 gram daily)	46	46
B.R. No. 51—Casein 18, Cornstarch 54, Lard 22, Cod Liver Oil 2, Salts 4, Yeast 0.4–0.6 gram daily	32	32
B.R. No. 51—Yeast 0.05 gram daily	2	2
B.R. No. 55—Casein (extracted) 18, Cornstarch 54, Lard 23, Cod Liver Oil 2, Salts 4, Yeast 0.4–0.6 gram daily	7	7
B.R. No. 59—Casein (extracted) 18, Cornstarch 54, Lard 15, Milkfat 9, Salts 4, Yeast 0.4–0.6 gram daily	4	4
F.F.P. 23—Casein 23, Cornstarch 73, Salts 4, Yeast 0.4–0.6 gram daily plus 2 drops Cod Liver Oil	5	5
B.R. No. 17—B.R. 67, Merrill Soule Whole Milk Powder 33	5	5
B.R. No. 27—B.R. 67, Skim Milk Powder 33	9	9
F.F.P. 18—Casein (extracted) 18, Cornstarch 76, Agar 2, Salts 4, Yeast 0.4–0.6 gram daily plus 5 drops Cod Liver Oil	3	3
F.F.P. 18 High Calcium—Casein 18 (extracted), Cornstarch 73, Agar 2, Salts 4, Calcium Lactate 3, Yeast 0.4–0.6 gram daily plus 5 drops Cod Liver Oil	4	4
F.F.P. 18 plus 1 drop Cod Liver Oil	6	6
B.R. No. 88—B.R. No. 51 with 5% yeast in Cup	5	5
TOTALS	180	180

In the above studies all criteria known to us have been employed. We have emphasized the fact that the normality of the females chosen had been proven in each individual instance. Matings took place on the occurrence of a precise stage in the oestrous cycle and the fate of "positive" matings followed by examination of the female for detection of the implantation sign (occurrence of erythrocytes in the upper vaginal canal from the fourteenth to the seventeenth day of gestation). Impairment in the spermatozoa does not in our experience lead to a transitory period characterized by their ability to fertilize yet with intrauterine failure of the young. Intrauterine failure is characteristic of the female sterility disease, but when sterility supervenes in the male there is no evidence of implantation in the female.

We have also studied the sex responses of males and analyzed the bouchon vaginale within a maximum of five minutes after its formation for the presence or absence of sperm and the detection of motility in the latter. These methods of study have enabled us to recognize broadly four stages

in the development of male sterility which may be enumerated as follows: (1) Normal abundance of sperm in the bouchon vaginale; loss of fertilizing power of the sperm;[3] approximately normal sex responses. Toward the end of this stage abnormal spermatozoa and instances of fused spermatozoa may be found. (2) Complete loss of sperm from the bouchon vaginale; sterility. Toward the end of this period our statistics show that less than half of all matings with oestrous females lead to a "positive" mating, whereas normally the proportion is over seventy per cent. (3) Loss of power to form the vaginal plug; there may or may not be a retention of sex responses. (4) Loss of all sex interest.

Male sterility is sooner or later characterized by grave changes in the seminiferous epithelium and in advanced cases by complete loss of that epithelium. For a long period of time, Leydig tissue is abundant.

Male sterility can be prevented by feeding from the day of weaning, in addition to the basic ration, certain single natural foods which have proven curative for female sterility. We have thus successfully employed a very potent substance, lettuce leaves, and two less potent ones, milk-fat and beef musculature. In the case of males born from mothers held upon the basic ration, the prevention of sterility may be similarly accomplished by the prophylactic use of foods. In these cases as well as in others we may also accomplish the same end by the prophylactic use of alcoholic or etheral extracts of certain beneficial foods. We have employed exclusively the ether extract of wheat germ. Six animals, for instance, have recently been studied with wheat germ oil, three receiving one drop daily and three six drops daily.[4] In the case of the single drop doses, fertility was retained for a period of about ten months, when sterility supervened. They were killed when thirteen months old and remarkably normal looking seminiferous epithelium still found. The animals receiving six drops daily preserved their fertility until the time they were sacrificed at thirteen months of age. The testes were normal. All of the brother littermate controls were sterile by the close of the fifth month and at thirteen months the seminiferous epithelium had practically disappeared.

We have found male sterility, once positively detected, difficult to cure, although proper prophylactic experiments are invariably successful. In our earlier work, cures were not usually attempted until from the fifth to the eighth month, at a time therefore when sterility was well advanced. The subjoined table will show that the administration of wheat germ oil at this time resulted in decisive cures, however, in about one-fifth of the cases. The animals were chosen from a large group and were in all cases controlled by brothers allowed to remain on the basic ration, in which group no instance of spontaneous recovery of fertility has been known to us. It is of interest that the cures were only secured after prolonged administration of the substance containing vitamine E, administration usually

for a period of three months; in one instance, indeed, fertility has first manifested itself after fourteen months of such curative regime.

CURES OF DIETARY STERILITY IN THE MALE WITH SIX DROPS OF WHEAT GERM OIL DAILY

DIET	NUMBER OF CURES			AGE OF RAT WHEN WHEAT GERM OIL WAS STARTED	TIME ON WHEAT GERM OIL BEFORE CURE WAS EFFECTED	NOTES
	CONTROLS	ATTEMPTED	SUCCESSFUL			
B.R. Yeast 0.4–0.6 gram daily	17	17	0	5–8 mo.		
B.R. No. 60 Yeast 0.2 gram daily	4	8	4	8 mo.	3–4 mo.	
B.R. No. 60 Yeast 0.4–0.6 gram daily	4	8	3	5–6 mo.	4–6 mo.	
B.R. No. 60 Yeast 0.8 gram daily	4	10	2	5–8 mo.	4–6 mo.	
B.R. No. 60 Yeast 1.6 gram daily	2	4	*1	8 mo.	14 mo.	*Only one litter to date
F.F.P. 18 plus 5 drops Cod Liver Oil	1	*2	0	7–8 mo.		
F.F.P. 18 High Calcium plus 5 drops Cod Liver Oil	1	*3	0	7–8 mo.		
F.F.P. 18 plus 1 drop Cod Liver Oil	1	*5	2	7–8 mo.	*1–3½ mo.	*Male sired one litter just before wheat germ oil was given although the 3 preceding positive matings were infertile
B.R. No. 51 Yeast 0.4–0.6 gram daily	2	*4	*0	5 mo.	*4 mo.	*To date
B.R. No. 88 (20 drops wheat germ oil)	2	*3	*1	4 mo.	*6 mo.	*To date
TOTALS	38	64	13	4–8 mo.	1–14 mo.	

* Male given wheat germ oil as soon as sterility was established.

In many cases before the initiation of the attempted cure, one testis was removed in order to ascertain the histological state of the organ and to make a comparison with the condition of the remaining organ when fertility had been induced. We attribute success in the restoration of fertility to the sporadic retention of bits of seminiferous epithelium in some tubules, although the majority of tubules were devoid of epithelium. The cure of dietary sterility was in all instances accompanied by an improvement in the sex response as well as by the regeneration of the epithelium in some tubules and development of normal fertilizing power of the sperma-

tozoa. It is interesting that the administration of the vitamine in the form of wheat germ oil has also resulted in a longer retention of normal sex responses in animals where the restoration of fertility was not accomplished. It has also led to superior growth, usually changing a growth plateau to the slow rise characteristic of the growth of males on natural foods. This general improvement could hardly be due to the "nutritional" value of the insignificant added substance. Since it was also present in cases which were not cured and in which the testicular epithelium had disappeared, it would seem a constitutional effect not mediated through the sex glands.

* Aided by grants from the Committee for Research on Sex Problems of the National Research Council and from the Bureau of Dairying, U. S. Department of Agriculture.

[1] Evans and Bishop, "On the Existence of a Hitherto Unrecognized Dietary Factor Essential for Reproduction," *Science*, December 8, 1922, see also *J. Metabolic Res.*, **3**, No. 2, February, 1923; and the *J. Amer. Med. Assoc.*, **81**, September 15, 1923.

[1a] We have adopted the letter E as the next serial alphabetical designation, the antirachitic artanine now being known as D.

[2] "Positive," used only for instances in which the occurrence of sexual congress was positively ascertained by the finding of sperm or the copulatory plug (bouchon vaginale) within eighteen hours after pairing such males with females of proven fertility and at the pro-oestrous or early oestrous stage.

[3] Such cases as we have been able to examine by the "fresh" method in this period (i.e., the period characterized by abundance of sperm with sterility) have always shown absence of motility in the sperm.

[4] In conjunction with Dr. George O. Burr, I shall later report upon the successful prophylactic employment of minute traces of a very concentrated fraction out of wheat germ oil, namely, the sterol-free or red oil portion of the non-saponifiable part of the original oil.

A HISTOLOGICAL STUDY OF STERILITY IN THE ALBINO RAT DUE TO A DIETARY DEFICIENCY

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In the winter of 1921–22, at the request of Dr. Osborne and Dr. Mendel, a thorough study was begun to determine the histological condition of the reproductive organs of rats fed artificial diets of known composition, adequate for growth but not for reproduction.

So far as we can find C. B. Paul[1] was the first to intimate that fertility is affected by diet. He states that "an excessive meat diet interferes with the development of the male reproductive organs" and that "the defective development is most pronounced in the seminal vesicles and prostate

gland." Hewer,[2] after excessive thymus feeding of rats, described a pronounced histological degeneration of the testes but normal conditions of the epididymis.

Funk and Douglas[3] next called attention to the atrophied testes and ovaries of pigeons suffering from beri-beri, but gave no evidence to show whether this condition was directly due to a deficient diet, or to the diseased condition of the birds.

Osborne and Mendel[4] noticed that although animals fed on their artificial diets "had grown vigorously to adult size they were, with very few exceptions, sterile." An examination of some of these animals, made by Allen,[5] showed "total degeneration of all the germ cells" in the testes.

Dutcher and Wilkins[6] found that "the testes of White Leghorn cockerels did not develop when the diet consisted of polished rice," but that "when supplemented with small amounts of green alfalfa atrophy of the testes did not occur."

After our own studies were begun Evans and Bishop[7] published a study of the effect of diet on the oestrous cycle. Meyerstein[8] reported histological differences between both the testes and ovaries of rats fed on diets low in the water-soluble vitamine compared with the corresponding organs of those receiving a larger quantity of this vitamine. Eckstein[9] found advanced degeneration of the testes but no evidence of abnormality of function in the ovaries of rats after feeding on diets poor in fat, vitamine A and phosphorus.

Evans and Bishop,[10] and other workers, have since shed much light on the female disorder and its relation to the reproductive vitamine. After learning that Evans and Bishop were studying the effect of diet on the female rat, the writer directed his attention to the male, with the results given in this paper.

Preliminary Work.—In the preliminary part of this work,[11] involving breeding tests, autopsies and histological studies of 20 male and 40 female rats reared under dietary regimes of several types, the following results were obtained: (1) No reproduction was secured in rats reared for 125 days or more on the standard casein diet (casein 18%, starch 54%, lard 15%, butter fat 9%, salt mixture[12] 4%), together with tablets of dried yeast, alfalfa, clover or dandelion, fed daily to supply a sufficient amount of water-soluble vitamine for normal growth. (2) A histological study of the ovaries showed a normal process of maturation and ovulation, followed by what seemed to be normal uterine implantation, although the embryos were aborted or resorbed in the late stages of gestation. (3) After prolonged feeding, the testes of the males were usually small and watery, and showed a degenerate histological condition. (4) Occasional reproduction was secured on a similar casein diet, containing egg yolk (casein 28%, starch 39%, lard 15%, butter fat 9%, salts 4%, egg yolk

5%, and tablets of 0.2 gm. of yeast fed daily). Excellent growth was obtained on both diets.

Experimental.—The purpose was to determine the period at which the degeneration becomes evident, the duration of the process, and the detailed histological and cytological changes involved.

The diet adopted as the basic ration in these experiments was casein 18%, starch 54%, lard 15%, butter fat 9%, salt mixture 4%, plus yeast tablets 0.4 gm. fed daily, which is successful in so far as the growth and vigor of the rats is concerned, although animals reared on this diet from the time of weaning never produce young. In the work done on recovery from sterility, this diet was supplemented with 40 gm. of fresh green lettuce fed daily, to supply the vitamine E. Of the 130 male rats used, 95 had one testis removed by operation (unilateral castration) before or after maintenance for various periods on the basic ration. After different periods of time the other testis was removed. Both testes of each rat were then studied histologically to determine the degree of degeneration after the different periods of dietary treatment, as well as the changes occurring in the same rat in the interval between these periods.

Results. (*a*) *Histology of the Testicular Degeneration.*—For convenience the degenerative process has been divided into five stages, as follows.

Stage 1. The mature sperm lose their individuality, clump together to form irregular masses or blotches of degenerate chromatin material, and are eventually passed off through the epididymis. Other stages of the spermatogenic process are still normal.

Stage 2. The sperm have disappeared in most of the tubules and the spermatids show a "beaded" appearance due to rupture of the nucleus and deposition of chromatin upon the nuclear wall. The cell walls of the spermatids seem to disappear towards the end of this stage, and the cytoplasm of the germinal epithelium segregates and rounds off in certain portions of the tubule preparatory to the formation of the giant cells of the next stage. The spermatocytes and spermatogonia appear normal. This stage is of very short duration, as indicated by its rather rare occurrence in the large number of testes studied.

Stage 3. The "giant cell" stage resulting from the segregation of rounded masses of cytoplasm in which are included from 2 to 40 degenerating spermatid nuclei. These multinuclear giant cells become pycnotic and eventually liquefy, possibly causing the rather watery condition of testes in this and later stages of degeneration. Many degenerate spermatids do not enter into the formation of the giant cells, but become detached and accumulate in large masses which are then passed to the epididymis. The spermatocytes usually show irregular clumping of the chromatin material on the nuclear wall. The cytoplasm of the epithelium becomes fibrous and vacuolated due to the sloughing off or dissolution of degenerate germ

cells and giant cells of all sizes. This stage is of relatively short duration.

Stage 4. A few giant cells in different stages of dissolution are usually present, along with spermatocytes and spermatogonia in stages of necrosis, although the latter are usually sloughed off from the germinal epithelium before degeneration is very marked.

Stage 5. Shows the histological condition of a cryptorchid testis. The germinal epithelium is reduced to a syncytium of Sertoli cells in a fibrous stringy layer of cytoplasm, which forms a thin layer near the periphery of the tubule or almost fills the inter-tubular space. The Sertoli cells and the interstitial cells show no degeneration, even in the most extreme cases. There is, however, a very marked shrinkage in the size of the tubules.

In advanced conditions the epithelium lining the ducts of the epididymis show changes indicating fatty degeneration.

(*b*) *Rats Reared on the Basic Ration from Weaning.*—After similar periods on the diet these rats, especially those from different litters, show wide variations in their testicular condition. The various types of degeneration reached at the different stages of dietary treatment are shown in Table 1. The animals were assigned to the several stages according to the condition of the majority of the tubules. None appear in the table under Stage 2 although in many cases some of the tubules were in the condition belonging to this stage. When sexually mature animals are fed on this diet this stage is more apparent, due to the slower degeneration of the testes.

TABLE 1

DEGREE OF TESTICULAR DEGENERATION IN RATS FED FROM WEANING ON THE BASIC RATION FOR 12 TO 150 DAYS

PERIOD OF DIETARY TREATMENT DAYS	NO. OF TESTES STUDIED	NO. OF NORMAL TESTES	NUMBER OF TESTES IN STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5
12– 40	4	4	.	.	.	.	.
50– 55	16	5	9	.	2	.	.
60– 65	15	6	8	.	.	1	.
70– 75	11	4	.	.	1	6	.
80– 90	14	1	4	.	1	7	1
100–150	12	.	.	.	.	4	8

The above data show that degeneration begins between 50 and 60 days after weaning, and that after 100 days on the diet degeneration is practically complete.

Table 2, based on Donaldson's figures for the normal, shows the relative weights of the body and testes.

TABLE 2

SHOWS BODY WEIGHT AND TESTIS WEIGHT (COMPUTED AS PERCENTAGE NORMAL BY WEIGHT) OF RATS REARED ON BASIC RATION AFTER WEANING

PERIOD OF DIETARY TREATMENT DAYS	NUMBER OF RATS USED	RATS % NORMAL BY WEIGHT (AVERAGE)	NUMBER OF TESTES WEIGHED	NORMAL WEIGHT OF TESTES (AVERAGE)	ACTUAL WEIGHT OF TESTES (AVERAGE)	TESTES % NORMAL BY WEIGHT
12– 40	4	148	..	....	....	....
50– 55	16	126	8	1.96 g.	2.12 g.	108
60– 65	15	122	14	1.99 g.	1.97 g.	99
70– 75	13	118	9	2.13 g.	1.61 g.	75
80– 95	16	118	14	2.25 g.	1.62 g.	72
100–150	12	128	5	2.67 g.	1.28 g.	44

(*c*) *Rats Fed on the Basic Ration after Attainment of Sexual Maturity.*—Sexually mature normal animals, varying in age from 60 to 105 days, were kept on the diet for 25, 50, 75 and 100 day periods before histological study of the testis. Table 3 shows that testicular degeneration is slower in asserting itself under such conditions, the critical period usually lying between 75 and 100 days.

TABLE 3

SHOWS THE DEGREE OF TESTICULAR DEGENERATION IN SEXUALLY MATURE RATS MAINTAINED ON THE BASIC RATION

PERIOD OF DIETARY TREATMENT DAYS	NO. OF TESTES STUDIED	NUMBER OF TESTES IN NORMAL	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5
25	5	5	.	.	.	.	.
50	12	11	1	.	.	.	.
75	10	7	1	.	1	1	.
100	11	1	3	2	.	.	5

(*d*) *Prevention of the Testicuar Disorder.*—Rats held on the basic ration until the testicular degeneration had begun, as determined by a study of one testis removed at operation, and then placed on the stock food diet (dog-biscuit plus carrots) for periods up to 75 days, show no improvement in the histological condition of the other testis, degeneration continuing as if no change had been made in the diet. If, after removal of one testis, the rats are given 40 grams of fresh lettuce daily, but kept on the basic ration for periods up to 150 days after operation, the second testis may show evidences of "partial prevention" provided some normal or practically normal seminiferous tubules were present at the beginning of lettuce feeding. Lettuce prevents the degeneration of such tubules, while those already in early and later stages of the disorder continue to stages of extreme degeneration. Of 36 rats, 20 in this series showed varying degrees of "partial prevention," but gave no indication that, once degeneration has set in, they can return to normal.

Lettuce fed from the beginning of the experiment prevents the testicular changes which would otherwise occur.

* The writer wishes to express his thanks and indebtedness to Dr. R. G. Harrison under whose direction the histological studies of this problem were carried out, at the Osborn Zoölogical Laboratory; and to Dr. T. B. Osborne and Dr. L. B. Mendel for their encouragement and coöperation in connection with the dietary work, the expenses of which were shared by the Connecticut Agricultural Experiment Station and the Carnegie Institute of Washington, D. C.

[1] Paul, C. B., *J. Physiol.*, 1906, **34,** p. XIV.

[2] Hewer, E. E., *J. Physiol.*, 1914, **47,** 479.

[3] Funk, C., and Douglas, M., *J. Physiol.*, 1914, **47,** 475.

[4] Osborne, T. B., and Mendel, L. B., *J. Biol. Chem.*, 1919, **38,** 223.

[5] Allen, E., *Anat. Rec.*, 1919, **16,** 93.

[6] Dutcher, R. A., and Wilkins, S. D., *Am. J. Physiol.*, 1921, **57,** 437.

[7] Evans, H. M., and Bishop, K. S., *J. Metabolic Research*, 1922, **1,** 335.

[8] Meyerstein, A., *Virchow's Arch. f. path. Anat. u. Physiol.*, 1922, **239,** 350.

[9] Eckstein, A., *Pfluger's Arch.*, 1923, **201,** 16.

[10] Evans, H. M., and Bishop, K. S., *J. Metabolic Research*, 1923, **3,** 233.

[11] The greater part of the results described under the heading "preliminary work" were obtained by Mr. J. T. Thompson, who was forced to discontinue his studies in May, 1922, on account of severe illness. The present writer took up the work in the autumn of that year.

[12] Osborne, T. B., and Mendel, L. B., *J. Biol. Chem.*, 1919, **37,** 572.

THE RELATIVITY DISPLACEMENT OF THE SPECTRAL LINES IN THE COMPANION OF SIRIUS

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The remarkable character of the companion of Sirius and the almost unique position it occupies as an object which might be expected to yield a very large gravitational displacement of the spectral lines on the theory of generalized relativity has been discussed in an interesting paper by Eddington.[1] In this article he has shown the extraordinary values of the density of the material composing the star which would follow as a consequence of a confirmation of a relativity displacement of the order predicted.

The possibility of deriving results of such interest for this star is, of course, due to the fact that it is at the same time a "white dwarf," that is, an early type star of very low intrinsic brightness, and a component of a visual binary system with well-determined elements. From the elements of its orbit its mass and velocity relative to the principal star may be derived, and the well-known parallax of Sirius in combination with the apparent magnitude of the companion provides a knowledge of its absolute magnitude. The spectral type of the star is a matter of direct

observation, and results for surface brightness, size and density follow as a consequence of what is known regarding stars of similar spectral class.

The first observations of the spectrum of the companion of Sirius were made at Mount Wilson with the 60-inch reflector in 1914[2] and showed that the spectrum was of an early type and not widely different from that of Sirius itself. The difficulties of such observations are evident. The brightness of the two stars is nearly in the ratio of 1 to 10,000, and at a distance of 10″ the scattered light of Sirius produces a spectrum which overlies that of the fainter star on all the photographs. Accordingly, it is necessary to select times of excellent seeing and to make the duration of the exposures as short as possible. For this reason the photographs obtained with the 100-inch reflector, with which the brightness of the fainter star relative to the illuminated field is greater than with the 60-inch telescope, are considerably superior. In the case of the more recent photographs diaphragms with circular apertures have been used to reduce the effect of the diffraction rays produced by the supports of the auxiliary mirrors. This has led to a marked improvement. All of the spectrograms have been made at the Cassegrain focus of the telescope at an equivalent focal length of 135 feet. A single-prism spectrograph with an 18-inch camera has been used for the observations, the average exposure time being about 40 minutes.

There seems to be little doubt that the spectrum of the companion is in some respects peculiar. The enhanced lines so prominent in the spectrum of Sirius are faint, λ4481 of magnesium being especially noteworthy in this respect. This agrees with the results found for other white dwarf stars. The arc lines are also faint, and the hydrogen lines form the principal feature of the spectrum. The distribution of the light in the continuous spectrum is noticeably different from that of the scattered light from Sirius and resembles that of an F-type star in being considerably more intense toward longer wave-lengths. As a result, the spectrum of the companion may be obtained nearly free from the spectrum of Sirius at $H\beta$, while at $H\gamma$ the superposition is very pronounced. At wave-lengths shorter than $H\delta$ the spectrum of the companion can hardly be seen upon that produced by the scattered light of Sirius. A consideration of these various features indicates that a classification of the spectrum as F0 is probably not seriously in error, although the line spectrum by itself would indicate a somewhat earlier type. It should be noted, moreover, that the increase in the amount of scattering toward shorter wave-lengths would tend to make the violet portion of the continuous spectrum from the scattered light somewhat more intense than in the case of Sirius itself. This may well account for a part of the difference observed. It seems probable, therefore, that the spectrum of the companion should be classed as earlier rather than later than F0.

For the purpose of measuring the relative velocities of Sirius and the companion a selection has been made of the spectrograms secured under the most favorable conditions and showing the spectrum of the companion most clearly. Four spectrograms have been found especially suitable, two of which are of exceptionally good quality. Since direct measurements are difficult on account of the diffuse character of the lines, they have been supplemented by an extended study and measurement of the two best spectrograms with the large registering microphotometer. For this purpose direct enlargements were made from the original negatives, and intensity curves of the more important spectral lines in both the spectrum of Sirius and that of the companion were traced with the microphotometer from these enlargements. The measurements, which were carried out by Miss Ware, who has had extensive experience with such photometric curves, consist in determining the centers of the chords of the curve of each spectral line at a large number of points between its base and vertex. The spectrum of Sirius lying on either side of that of the companion, the mean of the two curves for Sirius is compared with that of the fainter star. The horizontal scale of these curves is about 53 times that of the original negatives.

A second method of measurement makes use of the lines of the comparison spectrum as traced with the microphotometer. The curves of the lines in the spectrum of the companion are measured with reference to the curves of neighboring comparison lines, and the results are reduced by the usual method for stellar spectra after correction for the enlargement factor. The known radial velocity of Sirius is then subtracted from the value derived for the companion.

The spectrograms have also been measured directly with a comparator by one or more observers. In most cases only the spectrum of the companion has been measured and the resulting radial velocity has been compared with that of Sirius. Toward the violet end of the spectrum, however, it has been possible to measure some of the lines in both spectra and thus obtain differential values directly.

The following table gives the results of all the measures for the individual lines, the detailed values being listed in order to provide material for an estimation of the accuracy of the final results. The methods used in measurement are indicated and the relative displacements between the companion and Sirius are given for convenience as radial velocities in kilometers per second. The displacements in angstrom units may be obtained by dividing these values by 69 at $H\gamma$ and 62 at $H\beta$. The positive sign indicates a displacement toward the red of the lines in the spectrum of the companion relative to those in Sirius. The results for $H\beta$ and $H\gamma$ are entitled to by far the highest weight, the other lines being faint and difficult of measurement.

METHOD OF MEASUREMENT

PLATE NO.		COMP. *minus* SIRIUS KM./SEC.
	$H\beta$	
C776	Microphotometer	+31
C776	Microphotometer (Comparison lines)	23
C776	Comparator	24
C3110	Comparator	17
C3141	Comparator	31
C3156	Microphotometer	27
C3156	Microphotometer (Comparison lines)	28
C3156	Comparator	25
	$H\gamma$	
C776	Microphotometer	+13
C776	Microphotometer (Comparison lines)	17
C776	Comparator	2
C3141	Comparator	4
C3156	Microphotometer	8
C3156	Microphotometer (Comparison lines)	14
C3156	Comparator	12

ADDITIONAL LINES

λ	ELEMENT	PLATE NO.	METHOD	COMP. *minus* SIRIUS KM./SEC.
4215	Sr^+	C3156	Comparator	+4
4233	Fe^+	C3156	Comparator	5
4271	Fe	C776	Comparator	10
4290	Ti^+	C3156	Comparator	6
4300	Ti^+	C3156	Comparator	2
4404	Fe	C776	Microphotometer	37
4404	Fe	C776	Comparator	8
4481	Mg^+	C776	Microphotometer	20
4481	Mg^+	C776	Comparator	21
4549	Fe^+, Ti^+	C3156	Comparator	25

The outstanding features of these results are the definite character of the positive displacement and its change in amount with wave-length. The greater relative intensity of the spectrum of the scattered light of Sirius toward shorter wave-lengths and the increasing influence of the superposition of the lines in its spectrum upon those of the companion evidently will tend to reduce the amount of the measured displacement. Although the correction for this effect cannot be determined rigorously, some approximation to it can be gained from photometric measures of the relative densities of the continuous spectrum of Sirius and of Sirius *plus* companion at selected points throughout the spectrum. These have been made with the registering microphotometer and give the following values of the ratio of the photographic density of the continuous spectrum of the companion to that of Sirius at five regions in the spectrum:

λ4200	0.8	λ4400	1.2	λ4600	1.7
$H\gamma$	1.1	4500	1.4		

If we may assume, as seems justified from observation, that the relation

of line intensity to continuous spectrum is the same for the hydrogen lines both for Sirius and its companion, the above numbers will also represent the ratios of the intensities of the lines. For $H\gamma$, where the ratio is nearly 1, the measured displacement will require multiplication by a factor of nearly 2 to correct for the effect of superposition. At $H\beta$, on the other hand, the spectrum of Sirius is relatively so faint that no correction should be necessary. For the other lines the uncertainty is greater because the relationship of line intensity to continuous spectrum is probably different in the two stars. Under the same assumption as for the hydrogen lines, however, values for the correction factor may be found, when the displacement is small as compared with the widths of the lines, from the approximate formula

$$a = 1 + \frac{k_1}{k_2}$$

in which $k_1 = 1$ is the density of the spectrum of the scattered light of Sirius, and k_2 that of the companion. The correction factors would be larger the fainter the lines in the spectrum of the companion relatively to those in Sirius. Applying corrections obtained by this formula, and assigning double weight to the measures with the registering microphotometer on the hydrogen lines, we find the mean values

	KM./SEC.
$H\beta$	+26
$H\gamma$	21
Additional Lines	22
	+23

The relative velocity of Sirius and its companion may be computed readily from the elements of the visual orbit. For the mean epoch of the observations this is found to be 1.7 km./sec., the companion showing a motion of recession from Sirius. Applying this correction to the observed value, the final result for the displacement of the lines in the spectrum of the companion is +21 km./sec., or +0.32 angstrom. This value, interpreted as a relativity displacement, gives a radius for the star of about 18,000 km. If we use the values derived by Seares[3] for surface brightness, we find for the companion of Sirius, on the alternatives of F0 or A5 for its spectral type,

	F0	A5
Surface brightness	—0.88	—1.45
Radius (km.)	24000	18000
Density (water = 1)	30000	64000
Relativity Displacement (angstrom)	+0.23	+0.32

Eddington has calculated a relativity shift of 20 km./sec. on the basis of a spectral type of F0 and an effective temperature of 8000° for the companion. The resulting density is 53,000 for a radius of 19,600 km.

Although such a degree of agreement can only be regarded as accidental for observations as difficult as these, the inherent accord of the measurements made by different methods, and in particular with the registering microphotometer, is thoroughly satisfactory. The results may be considered, therefore, as affording direct evidence from stellar spectra for the validity of the third test of the theory of general relativity, and for the remarkable densities predicted by Eddington for the dwarf stars of early type of spectrum.

[1] *Monthly Notices*, **84**, 308 (1924).

[2] *Publications of the Astronomical Society of the Pacific*, **27**, 236 (1915).

[3] Contributions from the Mount Wilson Observatory, No. 226; *Astrophysical Journal*, **55**, 165 (1922).

THE BASIN RANGE PROBLEM

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Earlier and Later Views: King, Gilbert, Powell. The Great Basin of our Cordilleran region, including all of Nevada and parts of Utah, Arizona, California and Oregon, is occupied by many separate mountain ranges from 10 to 50 miles or more in length. They were explained 50 years ago by King in a then orthodox manner as the unconsumed residuals of much greater mountains that had been produced in late Jurassic time by the horizontal compression of a heavy series of stratified formations and their Archean foundation; and at about the same time in a then heterodox manner by Gilbert as eroded fault blocks, unequally uplifted on vertical fissures with more or less deformation but without horizontal compression. Gilbert's chief evidence for this novel view was based on a new physiographic principle, to the effect that if a mountain range has a relatively simple base line which transects the range structures, as he found to be the case in typical examples of the Basin Ranges, it must be limited by a fault, even though the down-faulted continuation of the transected structures in the adjoining less uplifted block cannot be seen by reason of its burial under the detritus eroded from the higher block.

Powell entered the discussion thus aroused by briefly announcing, apparently on deductive rather than observational grounds, that, before the production of the vigorous Basin Ranges by the dislocation and erosion of fault blocks, the Great Basin region had been degraded from the mountainous altitudes given to it by late Jurassic deformation and thereby reduced to "a comparatively low plain," thus implying a long erosional

period between what may be called, in this simplified statement of the problem, the King folding and the Gilbert faulting of the region; and implying also that this Powell surface ought to be, in some cases at least, recognizable in the tops or back slopes of the up-faulted ranges. Gilbert took no public part in this discussion, and only a small part in a later discussion when his fault-block scheme was rejected by Spurr; and although he revisited the Great Basin in 1901 and later years and modified his earlier views in several important respects, the results then gained were not published. The most significant of the later results was that, for certain ranges at least, the fault surfaces which he had originally assumed to be vertical were found to slant about 35°, and that the displacement of the fault blocks therefore not only did not involve any horizontal compression but demanded a considerable horizontal extension. In the meantime Louderback's studies of the Humboldt ranges in northern Nevada had shown, by his interpretation of the sheets of basalt that cover their back slopes unconformably, not only that they are tilted and moderately dissected fault blocks, as Gilbert thought, but also that, for those ranges certainly and for others by implication, Powell's deductive view was correct as to a long erosional period between the King folding and the Gilbert faulting.

During a recent visit to the Great Basin region, I had opportunity of examining several ranges, especially parts of the Wasatch, Oquirrh and certain others on the eastern side of the region, where Professors Schneider and Mathew of the University of Utah at Salt Lake City and Professor Hayes of Brigham Young University at Provo gave me much aid; also parts of the Sierra Nevada, Argus, Inyo, Panamint, Amargosa (east of Death Valley) and other ranges in southeastern California, where Mr. L. F. Noble of the U. S. Geological Survey gave me the benefit of his intimate knowledge of that large area. The results reached concerning, not the long geological history of the region, but the recent or physiographic origin of a number of the more vigorous ranges are in essence and in simplest form as follows:

Parts of the Argus range, east of the southern Sierra Nevada, and of the smaller Slate mountains next farther east, are unconformably covered on their back slopes by a thin sheet of basalt, now faulted, tilted and eroded with the range blocks; hence the rocks of these ranges must, like those of the Humboldt ranges, have been worn down to a Powell surface of small relief before the present ranges were formed. A similar conclusion, based on the simple profiles of their uplands, was reached for parts of the Oquirrh, Park Valley, Inyo, Amargosa and several other ranges. But it does not follow that all the Great Basin region had been worn down to "a comparatively low plain" before the present ranges were produced.

The simple base lines along parts of the Oquirrh, Inyo, Panamint,

Amargosa and certain other ranges transect their structures in so striking a manner as to assure their definition by great faults, and thus to confirm Gilbert's fault-block theory for these ranges at least. The same statement may be made for long stretches of the Wasatch mountains and the Sierra Nevada, but as those mountains constitute the borders of the Great Basin on the east and west, they should not strictly be included among the Basin Ranges; nevertheless, they afford excellent training ground for the study of ranges defined by faults, and the training there gained may be profitably applied to the study of ranges in the Great Basin proper.

The six ranges mentioned in the preceding paragraph, and also the little West mountain south of Provo, all appear to have suffered renewed and intermittent up-faulting of recent date along certain parts of their extent, whereby considerable areas of their previously buried fault surfaces are revealed along their margins. This renewed up-faulting measures several hundred feet in the Basin Ranges above named, and probably one or two thousand feet in parts of the Wasatch and the Sierra Nevada. The rock face in the upper part of the revealed fault surfaces is more or less dilapidated, but in the lower part it is almost intact; and the mountain-side valleys, which are maturely opened between rounded spurs aloft, are reduced to sharp-cut V-gorges in the middle part of the rock face, and are narrowed down to mere clefts at the mountain base; many of the stream clefts below the smaller upland valleys are not yet cut down to the mountain foot. In view of this small development of the valley mouths by the erosion of wet-weather streams, it is believed that the lower part of the rock surface between them has been very little affected by weathering; and hence that it closely represents the fault surface as revealed by the latest movements of up-faulting. Its inclination was repeatedly found to be only 30° or 40°; but it does not follow that all Basin Range faults have so small an inclination.

The recently revealed part of the fault faces now visible along the base of certain ranges may be 5000 or 10,000 feet below the Powell land surface of the time when the Gilbert faulting was initiated. Hence application may here be made of a principle enounced by McGee 40 years ago,[1] to the effect that, when profound faulting is initiated under certain conditions which are simulated by those obtaining in the Great Basin, the fault "must originate with normal hade in a deep-seated hypogeal couche, and . . . must be propagated upward with progressively diminishing hade, which may eventually become nothing or even reversed." That is, a slanting Basin-Range fault, as seen today, is a deep-seated part of a curved fault surface that may have steepened upward so as to be a vertical or overhanging fracture just below the surface of the land mass in which the fault was originally produced. Conversely, if a new fault were now originated in the recently revealed slanting face of a Basin Range, it might be seen as a

vertical fracture at the present surface, while deep below the surface it might be normally inclined to the down-throw; and some indications of such secondary vertical fractures were seen in the slanting fault face of the Wasatch and Panamint ranges.

The recent revelation of slanting fault surfaces has been accomplished not only by renewed up-faulting of the elevated side of a mountain block, as in Section 3, Fig. 1, but also by renewed down-faulting of the depressed side of the adjacent block, as in Section 4; for heavy detrital deposits sloping away from the mountain range must have been accumulated along a

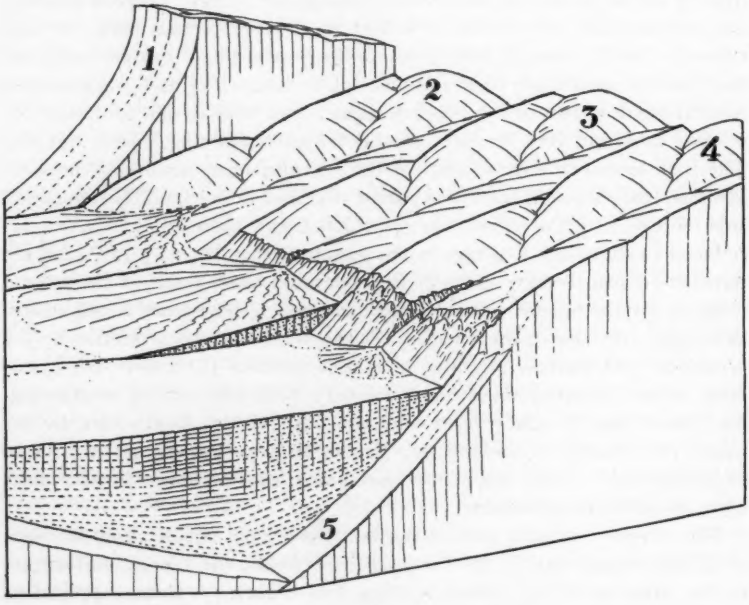

FIGURE 1

mountain border while its valleys were maturely eroded before renewed faulting, as in Section 2; and yet wherever fresh fault surfaces were found, they were adjoined, not by large detrital fans sloping away from the range, but, except where small, post-faulting fans have been very recently formed, by flat detrital plains, sloping gently toward the range and usually carrying saline pools close to the mountain base, as in Section 4; and the absence of detritus there may be taken as further proof that the lower rock face of the fault has not been significantly weathered back from a steeper slant since the last up- and down-faulting. Down-faulting of this kind appears

to have been more local than up-faulting. Blocks 1 and 5 in Fig. 1 represent the total potential displacement by faulting, never realized because of accompanying erosion.

The Oquirrh and the Panamint fault blocks appear to have suffered a slight rotation, for they show fresh fault surfaces of upheaval along parts of their western base, while the long and heavy detrital deposits that slope eastward toward the next range—the Wasatch and the Amargosa ranges, respectively—appear to have been given a slight increase of declivity by the down-faulting of their farther eastern parts in association with the recent up-faulting of those neighboring ranges. The V-gorges and the sharp clefts recently cut in the rock faces of the revealed fault surfaces on the west side of these two ranges in consequence of their upheaval may therefore be correlated with a moderate, down-grade furrowing of the detrital deposits on their eastern slopes in consequence of an increase in declivity there.

On the eastern or detrital back-slope of the Oquirrh range, where the furrows are several hundred yards wide and 100 or 200 feet deep near the mountains, bluffs were cut across the inter-furrow ridges and gravel spits were built across the furrows by the high-level waters of Lake Bonneville in Pleistocene time. The spits are so little modified that the erosion of the furrows in which the spits lie must have occupied an interval scores of times as long as the post-Bonneville epoch, which is generally thought to measure several tens of thousands of years. The erosion of deep valleys in the hard-rock mountains of the Oquirrh fault block and the associated deposition of the heavy and now furrowed body of detritus on its back slope must have occupied a period scores of times as long as the interval required for furrowing that slope; that is, this valley-erosion period must be measured by scores of scores of post-Bonneville epochs. And the final demolition of the Oquirrh range will demand an era many times longer than that of its valley-erosion period already elapsed; that is, a completed cycle of erosion, such as appears to have produced the Powell lowland surface previous to the Gilbert up-faulting of the Oquirrh and certain other Basin Range blocks, and such as will in time obliterate the present ranges, must be many times longer than scores of scores of post-Bonneville epochs. In other words, a cycle of erosion is roughly 2×10^7 or 2×10^8 years.

It is only the recently up-faulted range blocks that exhibit well preserved fault faces along their base: in those ranges, some of the fault faces are so recently revealed that their base line is fan-free between the fault-face gorges, although fan-based below the gorges, as shown in conventionally condensed form in Section 1, Fig. 2. In other ranges, a little older and more dissected, the V-canyons and clefts are deepened and widened, so that the originally little-incised fault face is divided into many spur-end

facets: there the accumulating detritus may rise high enough to enter the valley mouths and give the base line a fan-dented pattern, as in Section 2. With longer absence of renewed faulting the spur-end facets are rounded off, the valley mouths are enlarged and the margin of the range becomes fan-bayed, as in Section 3; but the spur ends may still stand nearly enough in line to suggest that their termination was originally defined by a fault. With yet longer quietude, the spur ends retreat irregularly from the fault line, their sides are carved by secondary valleys, and the mountain border becomes irregularly fan-frayed, as in Section 4; here the detritus in the fraying fan heads is a mere veneer on a beveled rock floor or pediment: it is by this time impossible to determine the original outline of the mass, and hence its original production by block faulting becomes uncertain. With more advanced erosion, detached spur ends become fan-wrapped as in Section 5; still later, the same term may be applied to the mountain itself, when it is reduced to monticules as in Section 6; and when the monticules

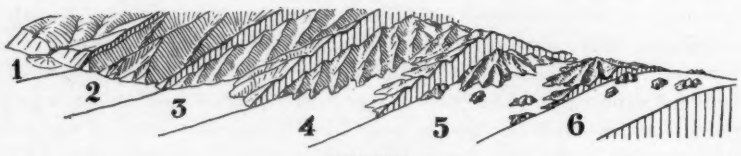

FIGURE 2

vanish, the dome-like residual mass may be described in Lawson's term as a pan-fan. Such domes are great rock masses sheeted with their own detritus; as time passes they will be very slowly worn down to less and less convexity. These changes will be delayed in resistant rocks and hastened in weak rocks; hence different stages of change may be found in different parts of a single range. Examples of all stages were noted in one or another part of the Great Basin. A good number of fan-wrapped monticules and some superb pan-fan domes, 5 or 10 miles in diameter and 2000 feet in height, were seen where California approaches the southern point of Nevada; but, as above intimated, it does not follow that those domes as well as various Great Basin mountains of straggling form, which are now in the older stages of degration with irregular margins, as drawn in Sections 4, 5, 6, originated in fault blocks, although such an origin seems well assured for the more continuous and vigorous linear ranges typified in Sections 1, 2, 3.

[1] W. J. McGee, "Origin and Hade of Normal Faults," *Amer. Journ. Sci.*, xxvi, 1883, 294–298.

THE SEPARATION OF RARE EARTHS BY THE IONIC MIGRATION METHOD

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The group of elements known as the rare earths comprises the elements of atomic number 57 to 71 inclusive, and yttrium with atomic number 39. These elements are distinguished by the extraordinary similarity of their chemical and most of their physical properties, a fact which renders their separation a matter of extreme difficulty. It is necessary, in practice, to take advantage of slight differences in solubility observed for corresponding salts and to resolve a given mixture into its components by a long series of fractional crystallizations or precipitations, ranging in number from several hundred to many thousand according to the elements present and the degree of purity desired. These operations are so laborious and time-consuming that chemically pure samples of individual rare earth compounds are practically unknown, save on the shelves of a few skilled workers in the field of atomic weights. The "rareness" of the rare earths is due not so much to the lack of abundance of their ores in nature as to the lack of a simple method for their separation.

In the course of our work in this laboratory on the attempted separation of isotopes by the ionic migration method,[1] the idea naturally occurred to us to extend the investigation to the rare earths, which approach isotopes so closely in similarity. Little is known of the relative mobilities of the rare earth cations in aqueous solution, but ionic volume and hydration variations within the group may be expected to induce differences in ionic mobilities which will, in most cases, exceed one per cent, so that a ready separation of a given mixture into its pure components should be, in general, feasible.[2] The experiments described below furnish, in fact, three instances of the successful separation of typical binary rare earth mixtures by the ionic migration method.

The principle of this method is, briefly, as follows. An agar-agar gel containing the given mixture is placed in a long glass tube, between similar gels containing a faster cation (nearer the cathode) and a slower cation (nearer the anode), respectively. On electrolysis, the two boundaries of the middle section remain quite sharp, even after the ions have travelled a long distance. If the two rare earth cations themselves possess appreciably different mobilities, the faster ion will gradually accumulate in the forward portion of the sample, while the slower ion will be relegated to the rear, so that separation may be effected by slicing up the gel at the conclusion of the run. For further details, and for a diagram of the apparatus

employed, the earlier communications referred to above should be consulted.

So far as we can discover, the application of this method to rare earth separations is entirely new. The only related suggestion found in the literature is in an article by Jules Roux[3] in 1908. This author states, after some questionable calculations on the mobilities of some rare earth cations from salt conductivities, as follows: "This is very important. It is well known that the rare earths are very difficult to separate: one can conceive, on account of this great difference in mobility, of the possibility of making this separation either by diffusion or by electrolysis."

Experimental.—Before any actual separation of rare earths could be attempted, it was necessary to perform a large amount of preliminary work to obtain data on the following points:

(*a*) *Choice of preceding and following ions.*—The first selection for a preceding ion was obviously hydrogen, on account of its high mobility. It soon became evident, however, that a gel containing any practicable concentration of hydrogen ion had lost its power of setting. Ammonium was next tested and proved more satisfactory, but was later discarded in favor of potassium, since a good gel could not be obtained with ammonium in concentrations greater than 0.3 *N*. Sodium was found to be inferior to potassium in stability of gels as well as in ionic mobility.

A suitable following ion requires to possess a mobility as far below those of the rare earth cations as possible. No trustworthy data were available in this connection, but by analogy from the periodic curves of Bredig[4] it appeared most likely that trivalent ions of low atomic weight would meet the requirements. The first experiments were therefore made with aluminium and chromium. In both cases a good rear boundary was maintained, showing that the difference in mobilities was adequate and in the right direction. Chromium possessed the advantage over aluminium of giving a sharp color boundary, and was employed in all the final runs.

Trouble was constantly experienced, however, with chromium in the system, for several reasons which will appear in subsequent paragraphs.

(*b*) *Length and concentration of rare earth section.*—The shorter the section, the shorter the length of run and the time necessary to effect a complete separation. On the other hand, enough material must be taken to secure several slices for analysis, each containing a quantity of salt sufficient for the analytical method. After some trials, it was decided to use a section 8–10 cm. long, with a total rare earth concentration of 0.4–0.5 *N*. At the end of a run, this was cut into slices 1 cm. thick. The internal diameter of the tube being about 3.7 cm., the volume of each sample was thus approximately 10 cc.

(*c*) *Concentrations of preceding and following ions.*—The length of the rare earth section remains constant only if definite concentration ratios

of the respective salts are employed in the adjacent gels. Equilibrium is established at a boundary when $C/T = C'/T'$, C and C' being the equivalent concentrations and T and T' the transference numbers of the two cations concerned.[5] The success of the ionic migration method depends, to a large degree, upon the proper adjustment of salt concentrations in the various gels in accordance with this rule.[6]

No transference ratios for the rare earth cations being on record, it was necessary to resort to trial. A concentration of 0.6–0.7 N proved to be perfectly satisfactory for the preceding gel, with potassium chloride as solute, the front boundary remaining perfectly sharp throughout the runs. With chromic sulfate in the rear section, however, it was found impossible to prepare a gel with a concentration higher than 0.2–0.3 N. This was evidently insufficient, since the rear boundary invariably became blurred during the first day of the run. Automatic adjustment of concentration at the boundary, however, fortunately caused a rapid subsequent recovery of sharpness. It is of interest to note that the very dark color of the chromium gel thus built up just behind the boundary indicated a concentration considerably higher than any obtainable by the ordinary method of preparing the gels.

(*d*) *Preparation of the gels.*—Various concentrations of agar-agar were tried out, and a 2 per cent gel was found most suitable. The properties of the gels proved to be very markedly dependent upon the mode of preparation, the previous heat treatment, etc. The method generally employed was to mix equal volumes of agar solution and salt solution at the boiling-point, setting taking place spontaneously as the gel cooled. In the case of chromic sulfate, however, which is considerably hydrolyzed at high temperatures, the salt and agar solutions were not mixed until both had cooled to 60°, and the mixture was made to set by means of ice-water. It is noteworthy that this empirically-determined temperature, 60°, could not be varied more than a few degrees without obtaining a mixture which refused to set under any circumstances. The concentrated chromium gel formed at the rear boundary during a run also refused to reset after once being melted.

(*e*) *Rate of movement of the boundaries.*—The speed at which the boundaries move depends upon the concentration of the solutions and the potential difference between the electrodes. The higher the voltage employed and the lower the concentration, the more rapid the migration. It is desirable to have the boundaries move as fast as possible, since this shortens the time required for a run and minimizes the opposing effect of diffusion. Limits are imposed, however, by the fact that the concentration used must be great enough for analytical accuracy, and by the heating effect of the current. With the apparatus set up as described in previous articles and the concentrations given in (*b*) and (*c*) above, a 240 volt cur-

rent caused a movement of about 20 cm. a day, the tubes being kept cool by immersion in a trough of running water. The amperage averaged 0.6–0.8 during the run.

(*f*) *Electrode liquids.*—Provision must be made at the electrodes for supplying to the gel the ion which is being removed by the electrolysis, and for neutralizing the hydrogen and hydroxyl ions produced at the anode and the cathode, respectively.

This was accomplished at the cathode by using a hydrochloric acid solution, changed daily as it approached exhaustion. At the anode a paste of precipitated chromic hydroxide (prepared by adding ammonia to a boiling solution of chromic sulfate or chrome alum, and washing with hot water until free from ammonium ion) was employed. A solution of chromic sulfate served as the electrode liquid, and this also was changed daily. (Later work by Dr. Eric R. Jette has shown that much more satisfactory results are obtained by mixing a fine meal of chromic sulfate crystals with the chromic hydroxide, so maintaining a saturated solution throughout.)

(*g*) *Method of following the boundaries.*—When one of the solutions at a boundary was colored, its position could, of course, be easily followed by the eye. Frequently it was possible to note the boundary between two colorless solutions visually by the difference in refractive index, but this could not be depended upon at all times.

A very simple and reliable method was devised for such cases, based on conductivity differences between the various solutions. Through the rubber connection between two of the lengths of glass tubing two small platinum wires were inserted, and these were made the electrodes of a small conductivity set. Readings were taken at intervals when a boundary was suspected to be nearing the point, and the time of passage was unmistakably signalled by a marked change in the bridge reading.

With certain mixtures, not only the position of the boundaries of the rare earth section, but also the actual progress of the separation within this section, could be very conveniently observed by means of a small direct-vision hand spectroscope. The majority of the rare earths give characteristic absorption spectra, consisting of readily distinguishable sharp lines. The exact location of a given element in the tube could consequently be determined during a run by moving the spectroscope parallel to the tube and noting the points of appearance and disappearance of these lines. When two spectra-producing elements were present, the gradual variation in the relative intensity of the lines due to each as the spectroscope was moved from the rear to the forward boundary gave an immediate indication of the extent of the separation at any stage of the run.

The three separations attempted may now be briefly described.

1. *Yttrium-Erbium.*—The sample employed was kindly furnished to

us by Professor Charles James, of the University of New Hampshire, to whom we are indebted for many valuable suggestions in this work. It contained yttrium and erbium in the form of oxalates in the approximate atomic ratio of 1 to 3, no other rare earths being present in significant quantity. The oxalates were converted to chlorides by ignition in a platinum crucible and solution of a weighed sample of the resultant oxides in hydrochloric acid.

Several runs were made, with practically identical results after the technique had been mastered. The following are the details regarding a typical run, No. 15: 0.7 *N* potassium chloride; 0.5 *N* total rare earths; 0.2 *N* chromic sulfate; 2 per cent agar-agar throughout. Time of run, 14 days; distance of run, 193 cm. The gel was sliced immediately, and eight samples were found to contain rare earths. These were placed upon covered watch-glasses, dehydrated in an electric oven at 120° for 48 hours, transferred to platinum crucibles, powdered and ignited to remove all organic matter. The rare earth residues were brought into solution by addition of dilute hydrochloric acid, and filtered off from the insoluble agar ash. Excess acid was eliminated by evaporating almost to dryness, or by addition of ammonia. The solution was diluted, heated to the boiling point, and oxalic acid (or potassium oxalate) solution added in excess. The mixture was allowed to stand for 24 hours and the precipitated solutes were then filtered off, washed thoroughly with boiling water, dried at 110°, and ignited to constant weight to obtain the oxides.

These were then analysed by the method of Wild.[7] A weighed quantity (0.1–0.2 g.) of the mixed oxides was dissolved in a measured excess of 0.2 *N* sulfuric acid (standardized against pure sodium oxalate). To the solution excess of *N* potassium oxalate solution was added and the excess sulfuric acid titrated with 0.1 *N* sodium hydroxide solution (free from carbonate, standardized against pure benzoic acid), phenolphthalein being employed as an indicator. From this the "mean atomic weight" of the rare earths in the sample could be calculated, and hence the percentage of each component present. The results are tabulated below. The sections are numbered from the forward boundary; Sample 1 was unfortunately lost.

SAMPLE NUMBER	H_2O_2/H_2SO_4	MEAN ATOMIC WT.	PER CENT Yt
2	0.784	91.2	97.1
3	0.801	93.7	93.9
4	1.013	124.8	54.4
5	1.138	143.3	31.0
6	1.174	148.6	24.2
7	1.191	151.0	21.2
8	1.189	150.8	21.4
Original mixture	1.157	146.0	27.5

Duplicate determinations and check runs upon pure oxide samples showed that the method was accurate, under the conditions of experiment,

to about 1 per cent. Analyses made upon the original mixture in the presence and in the absence of agar gave concordant results, showing that the ash of the incinerated gel did not introduce any significant errors into the method of analysis. Similarly the presence of potassium and chromic salts was found to have no disturbing effect.

The results demonstrate then an accumulation of yttrium (at. wt., 88.9) in the forward samples, increasing the percentage of that element from 27.5 to 97. The extent of separation in the rear sections was not so marked, the percentage of erbium (at. wt., 167.7) increasing only from 73.5 to 79. This was considered as probably due to the unavoidable concentration changes at the chromium boundary, discussed in (*c*) above. There was also the possibility that the distance of the run was insufficient for complete separation.

In a later run, a 3 cm. rare earth section was moved 390 cm. in 21 days, and the first and last samples were analysed. The first gave a mean atomic weight of 89.6, corresponding to 99.1 per cent yttrium; the last gave a mean atomic weight of 164.0, corresponding to 95.3 per cent erbium. It is evident, therefore, that an almost perfect separation of these elements may readily be obtained by this method.

A rough idea of the extent of the separation, in fact, could be obtained during the course of each run by observing the characteristic lines in the erbium absorption spectrum. The color of the precipitates also varied progressively from pure white at the yttrium end to light rose at the erbium end.

2. *Neodymium-Praseodymium.*—For this notoriously difficult separation, large well-formed crystals of neodymium nitrate and praseodymium sulfate were secured from the Chandler Chemical Museum of Columbia University. An examination of the absorption spectra in each case indicated a very high state of purity, none of the numerous and persistent lines for either element being visible in the spectrum of the other. An equimolecular mixture was made up, and a run carried out under the same conditions as in the previous separation. In 19 days the boundaries were moved 390 cm., and a pronounced color change had become visible in the sample, the forward portion being distinctly green and the rear portion purplish.

Methods for the determination of mean atomic weight from the mixed oxides are not applicable to this pair of rare earths, both because of the very slight difference between the two elements and because of the fact that praseodymium salts give not only Pr_2O_3, but also variable quantities of PrO_2 and Pr_4O_7 on ignition. For the purposes of this work, however, the visible color change and the marked variation in the intensity of characteristic lines along the length of the section sufficed to demonstrate conclusively that a considerable degree of separation had been achieved.

For more careful spectroscopic examination, the section was sliced up and the two end samples ignited. The residues were treated as described in the yttrium-erbium separation to obtain the rare earth oxides free from agar ash, and these were then converted into the nitrates and allowed to crystallize. From the forward section, green crystals were obtained, which showed the characteristic lines of praseodymium very sharply and the most persistent lines of neodymium only very weakly. The rear section gave crystals decidedly pink in color, in which the relative intensities of the two spectra were reversed.

3. *Gadolinium-Samarium.*—Samples of gadolinium oxalate (containing about 0.2 per cent of erbium) and of samarium oxalate were obtained from the Welsbach Company. An equimolecular mixture was made up, and a run of 401 cm. carried out in 18 days under the conditions already described. To test the extent of separation, the same analytical method was followed as in the case of yttrium-erbium. The atomic weights of the two elements are too close together to make the analysis anything more than a rough approximation, but no trustworthy evidence could be derived here from color differences or absorption spectra. Samarium gives, it is true, several weak lines, but these could be observed only with difficulty under the very best conditions of working.

Only the first and last samples were tested, duplicate determinations being made. The "mean atomic weights" of the rare earths obtained from the front sample were 156.1 and 156.3, the average value 156.2 indicating a large excess of gadolinium (at. wt., 157.3). For the rear sample the figures were 151.4 and 152.3, the average value 151.8 indicating the predominance of samarium (at. wt., 150.4). Incidentally it was noted, in the course of the analytical work, that the oxide from the rear sample dissolved very readily in cold acid, while the oxide from the front sample required prolonged digestion with a large excess of hot acid before solution was effected. This agrees with the report in the literature[8] that Gd_2O_3 is difficultly soluble in acids, while Sm_2O_3 is easily dissolved.

Summary.—The experimental technique for the application of the ionic migration method to the separation of rare earth mixtures has been developed in detail, and the separation of three typical pairs of rare earth elements: (1) yttrium-erbium; (2) neodymium-praseodymium; (3) gadolinium-samarium has been attempted. In all three cases a very considerable degree of separation was rapidly achieved, and the results obtained leave no room for doubt that the method would give, with longer runs, perfect separation for all mixtures in which the ionic mobilities of the components are significantly different.

It may be mentioned, in conclusion, that the ionic migration method is now being applied to a zirconium-hafnium mixture, kindly supplied to us by Professor Hevesy, in the hope of isolating pure hafnium thereby.

Investigations are also being carried out upon potassium and rubidium, in order to test out the conjecture that the weak radioactivity of these elements is due to the presence of minute traces of the unknown alkali element with atomic number 87.

* Contribution No. 470.

[1] Kendall and Crittenden, *Proc. Nat. Acad. Sci.*, **9** (1923) 75.

[2] Kendall and White, *Proc. Nat. Acad. Sci.*, **10** (1924) 458.

[3] Roux, *Compt. rend.*, **146** (1908) 174.

[4] Bredig, *Z. physik. Chem.*, **13** (1894) 191.

[5] Noyes and Sherrill, *Chemical Principles*, 1922 (108–9).

[6] MacInnes and Smith, *J. Amer. Chem. Soc.*, **45** (1923) 10.

[7] Wild, *Z. anorg. Chem.*, **38** (1904) 191.

[8] Spencer, *The Metals of the Rare Earths*, 1919 (121, 141).

A NOTE ON THE PRINCIPLE OF DETAILED BALANCING

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Communicated May 25, 1925

An interesting note by Professor G. N. Lewis[1] in a recent number of these PROCEEDINGS invites perhaps some supplementary comments. The principle of "entire equilibrium" or the law of "reversibility to the last detail" there enunciated, seems certainly likely to prove of very great importance in chemical investigations. It may therefore perhaps be helpful to readers of Professor Lewis's note to call attention to the considerable amount of recent work in physics, in which this principle has been developed or exploited in the last few years, under the name (among others) of the "principle of detailed balancing." It seems unnecessary that the relevant parts of these investigations should be worked through anew.

As Professor Lewis himself dimly hints, modern formulations of the principle of detailed balancing really all derive their inspiration from a classical paper by Einstein[2] written in 1917. The earliest modern formulation of the principle may perhaps be attributed to O. W. Richardson.[3] The next step in the development is the well-known paper by Klein and Rosseland[4] in which the idea is applied to the mechanism of inelastic impacts of electrons with atoms. It is there deduced that there must also be superelastic impacts or "collisions of the second kind," in order to balance these inelastic impacts in detail. Thus an electron colliding with an excited atom may come off with increased energy, having acquired as kinetic energy the energy of excitation of the atom, leaving it in a state of lower energy. This idea has proved of the utmost value in the theoretical

discussion of a great number of phenomena for which one may refer to papers by Franck and Cario.[5]

This application has been followed by many others. The process of ionization and recombination in collisions has been discussed on the same principle by Fowler[6] and applied to the phenomena of the capture and loss of electrons by α-particles moving at high velocity. The theoretical discussion has been extended to molecular collisions. The photo-electric process of ionization and capture has been discussed independently, on the same principle, by Milne[7] and Kramers,[8] and both types of process have been considered (also independently) by R. Becker.[9] Eddington,[9a] in his investigations of the stellar absorption coefficient, had previously made implicit use of the same principle. This even is not all, for Pauli[10] and Einstein and Ehrenfest[11] have discussed, with the aid of the same principle, the laws of the Compton-Debye mechanism of the scattering of radiation by single electrons. The latter discussion deals with more general elementary processes, in which any number of quanta are absorbed and any other number of quanta are re-emitted. Finally Dirac,[12] using again the same principle, has formulated the laws of the most general process in which the collision of any number of bodies and the absorption and emission of any number of quanta may be concerned. It is interesting to note in conclusion that the principle is really a natural explicit extension of the ideas of Kirchhoff.[13]

These examples may suffice to show that physicists have been by no means blind to the probable importance of the principle of detailed balancing or entire equilibrium, that progress in the formulation of the laws of mechanisms has been made by its means, and that successful applications have been made to many phenomena. It is therefore all the more interesting that we are promised a series of investigations by Professor Lewis on the mechanisms of chemical reactions. The principle has in fact already been applied in this connection in a paper by Christiansen and Kramers[14] on the theory of mono-molecular gas reactions. But very much more must be waiting to be done on the chemical side.

[1] G. N. Lewis, these PROCEEDINGS, March (1925), p. 179.

[2] Einstein, *Phys. Zeit.*, **18**, 121 (1917).

[3] O. W. Richardson, *Proc. Phys. Soc. London*, **36**, 392 (1924), referring to *Phil. Mag.*, 27 (1914), but there is only rather a vague statement of the principle in the earlier paper.

[4] Klein and Rosseland, *Zeit. Phys.*, **4**, 46 (1921).

[5] Franck, *Zeit. Phys.*, **9**, 289 (1922). Cario, *Ibid.*, **10**, 185 (1922). Cario and Franck, *Ibid.*, **11**, 161 (1922); **17**, 202 (1923).

[6] Fowler, *Phil. Mag.*, **47**, 257, 415 (1924); *Proc. Camb. Phil. Soc.*, **22**, 253 (1924).

[7] Milne, *Phil. Mag.*, **47**, 209 (1924).

[8] Kramers, *Phil. Mag.*, **46**, 836 (1923).

[9] R. Becker, *Zeit. Phys.*, **18**, 325 (1923).

[9a] Eddington, *Monthly Notices R. A. S.*, **83**, 32 (1922); also **84**, 104 (1924).

[10] W. Pauli, Jr., *Zeit. Phys.*, **18**, 272 (1923).

[11] Einstein and Ehrenfest, *Zeit. Phys.*, **19**, 301 (1923).
[12] Dirac, *Proc. Roy. Soc.*, **A 106**, 582 (1924).
[13] Kirchhoff, *Pogg. Ann.*, **109** (1868). Translated in Scheiner's *Astronomical Spectroscopy*, Frost's translation, 1894, p. 113.
[14] Christiansen and Kramers, *Zeit. Phys. Chem.*, **104**, 451 (1923).

THE MEASUREMENT OF THE ABSOLUTE CHARGE ON THE EARTH'S SURFACE

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The existence under normal weather conditions of a potential gradient of the order of 100 volts per meter has been demonstrated experimentally.[1] The direction of this gradient indicates a negative charge upon the earth's surface in accordance with the well-known equation

$$4\pi\sigma = -dV/dn$$

connecting the charge density on a surface with the potential gradient near the surface and such a charge has been commonly assumed to exist. It is conceivable, however, that a distribution of electricity could exist in the atmosphere which would give rise to the potential gradient without a negative charge on the earth's surface.

In order to verify the existence of this charge, measurements were begun in September, 1924, and have been continued until the present time.[2] The method used is simple in principle. A horizontal plate mounted on an insulator just above the surface of the ground is momentarily earthed. A second plate which is in contact with the earth is then superposed. The charge on the first plate now seeks to escape according to the principle demonstrated by Faraday that a charge will not remain in the interior of a conductor. If the earth's surface is neutral, i.e., if the electrons are present in number equivalent to the positive charge on the atomic nuclei, no effect is to be anticipated.

The charge on the plate may be detected either by an electrometer or galvanometer. During the winter months when the atmospheric conditions were favorable an electrometer was used. When the weather became warmer and dampness caused trouble in insulation, a ballistic galvanometer was substituted.

In its final form the apparatus consists of two stationary quadrants of approximately 0.6 square meter area and two moving quadrants of equal dimensions which are rotated in such a way as to alternately cover and

expose the fixed quadrants. The fixed quadrants are mounted on insulators a few centimeters above the ground and are connected to the ground through a ballistic galvanometer. The moving quadrants are grounded directly and are rotated in synchronism with the period of the galvanometer by a motor. As the fixed quadrants are covered by the moving plates the charge flows off through the galvanometer to the ground. As the fixed quadrants are again exposed the charge flows back. The galvanometer is thus set in oscillation and its amplitude builds up until the ballistic impulse of the current is balanced by the damping of the moving coil. From the logarithmic damping factor and the maximum swing the deflection corresponding to a single discharge is readily calculated. The largest oscillations of the galvanometer observed were 20 to 30 millimeters, corresponding to a single deflection of 0.8 mm. and 4×10^{-10} coulombs of electricity. The plates are made of copper and the galvanometer circuit is open and contains no switches or moving parts. Elaborate tests were made to determine the effect of contact differences of potential between the various parts of the apparatus, and the ground by applying potentials with a battery of dry cells. As was anticipated no effect was produced by a potential between the ground and the apparatus as a whole, but a potential between the fixed and moving quadrants affected the deflection. One volt produced an effect which was barely noticeable and since the moving and fixed quadrants were of the same material and connected by a metallic circuit it is not believed that appreciable error could be caused by contact potentials.

The apparatus was mounted at a considerable distance from any building.

The results of the measurements indicate that the ground is charged negatively during fair weather, the amount of the charge fluctuating considerably. No particular difference was noticed between day and night except that the largest deflections appeared to be observed on bright sunshiny days. The average charge density is of the order 10^{-10} coulombs per square meter, which is probably sufficient to account for the potential gradient in the atmosphere that would be obtained under corresponding weather conditions.

No variation was observed during the partial eclipse of the sun in January, 1925. At the beginning of a rainstorm, however, the charge drops to zero and even becomes slightly positive. This observation has been made repeatedly and confirms the observations on potential gradient.

In order to calculate the potential of the earth relative to a point in free space it would be necessary to make some assumption as to the electrical condition of the upper atmosphere.

C. T. R. Wilson[3] demonstrated the existence of a positive current in air flowing downward to the ground, tending to neutralize the negative charge.

The source from which the negative charge is continually renewed appears to be a mystery, unless there be downward negative currents at the poles.

The apparatus described above could easily be modified so that its sensitivity would be greater. It could be operated continuously in all kinds of weather with self-recording instruments. It appears that the measurement of the charge by the foregoing method might have advantages from the practical standpoint over measurements of potential gradient and the data should be equally significant.

[1] Humphreys, "Physics of the Air," Lippincott (1920).

[2] An article describing some work along this line by Ramsauer (*Ann. Physik.*, **75**, 449 (1924)) came to the attention of the authors shortly after they had begun their work. Ramsauer used a method identical in principle with theirs and his results are in general agreement but he apparently made only a limited number of observations.

[3] *Proc. Roy. Soc. London*, **80A**, 537 (1908).

FOSSIL PLANTS FROM THE TERTIARY OF PATAGONIA AND THEIR SIGNIFICANCE

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No Neogene fossil plants have ever been recorded from Patagonia. A collection made by Dr. Burton Clark from Mirhoja, Chubut Territory, in 1923 (Lat. 44°20′S., Long. 70°W.) contains 36 determinable forms and is chiefly interesting in the bearing which it has on the environment of the extensive and remarkable terrestrial fauna of the Santa Cruz formation.

The plants represent the following genera, several of which have been previously unknown as fossils: Myrica, Celtis, Lomatites, Peumus, Leguminosites, Erythroxylon, Icica, Schinopsis, Maytenus, Sapindus, Schmidelia, Cupania, Rhamnidium, Malvacarpus, Sterculia, Tetracera, Banara, Nectandra, Myrcia, Styrax, Arrabidaea, Bignonites, Strychnos and Faramea.

All are distinctly American in their facies and show no traces of African relationships and therefore tend to disprove the hypothesis of Lydekker and others that the peculiar mammalian fauna of Patagonia was derived via a landbridge connecting this region with Africa.

The plants are well preserved in a water laid tuff, and show sufficient similarities to the stratigraphically precisely located flora from the Arauco district of Chile[1] to enable their age to be determined as Miocene. All are Dicotyledonous arborescent forms or lianas except a single unidentified grass. They do not resemble the existing flora of the open woodlands

and savannas that extend southward from about Lat. 30° in a narrow belt through the pampas of the provinces of Las Pampa and western Buenos Aires to about Lat. 38°.

They are also strikingly different from the rainforests of southern Chile, which occur in Argentine territory along the Andean margin in the western edges of Neuquen, Rio Negro, Chubut and Santa Cruz, and which consist largely of evergreen beeches and conifers. They are entirely unlike the flora of the drier Chaco and Quebracho regions dominated by various scrubby Leguminosae and which at the present time cover most of northern Argentina west of the Parana and Paraguay rivers, but they do show resemblances to the wetter Chaco flora near those rivers (Formosa), and to the flora of the Argentine Mesopotamia (Entre Rios, Corrientes and Misiones), which reaches its present southern limit at about Lat. 33°.

They indicate a mild and genial warm temperate climate with abundant rain. At the present time the country between latitudes 40° and 52° is in the rain shadow of the Andes. The indications of a greater rainfall at the time the fossil flora flourished, as well as its resemblance to the flora of approximately the same age at about the same latitude in Chile indicates that the Andes of that time, if they existed at all as mountains, were sufficiently low and broken to permit the interradiation of the floras and to permit the access of the moist westerly winds.

In the restorations of Professor W. B. Scott the Santa Cruz mammals are invariably depicted in a semi-arid plains country, and in his discussions he states that Patagonia at that time, although having a much milder and more genial climate than at present, appears to have been a country of open plains with few trees. It is true that arboreal forms of mammals are rare, but a few monkeys have been discovered, and ground sloths are exceedingly abundant. For the absence of aquatic reptilia or arboreal sloths I have no explanation to offer unless it be due to accidents of preservation or discovery, and although the variety and abundance of peculiar ungulates indicates considerable stretches of open country, it is clear from the associated plants that this country was not like either the present pampas or the savanna country, but contained large areas of well developed forest of a somewhat subtropical facies.

The leaves are broad and mesophytic, one being 20 centimeters in diameter, and where the fossil genera are represented in the present Chaco, as for example in Celtis, the fossil species are large and similar to Brazilian species and not like the reduced forms of the Chaco.

The fossil flora has been fully studied and the complete account of it will appear in the Hopkins Studies in Geology.

[1] Berry, E. W., *Johns Hopkins University Studies in Geology*, No. 4, pp. 73–144 (1922).

HUMAN BLOOD GROUPS AND THEIR BEARING ON RACIAL RELATIONSHIPS

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Communicated May 20, 1925

A comparative study of the literature shows that in any race there seems to be a definite proportion, characteristic of that race, of the four human blood groups; and that the differences between various races in the proportions of the groups are of such nature as to warrant the assumption that the variations in group proportions may constitute a valuable method of studying racial relationships. Contrary to some of the statements found in the literature, the recessive agglutinins appear to be the primitive condition, from which the dominant agglutinogens arose by mutation. These dominant agglutinogens appear to have arisen separately, in different regions, and to have been brought together by mutual infiltration of the races bearing them.

Various races in all parts of the world have been studied for their blood group proportions by many investigators, but little or no attempt has been made to correlate these observations. There are very many races as yet unstudied, but enough work has been done to suggest that the varying degree of occurrence of the two factors concerned may indicate something of the racial relationships.

Studies are now being made by the writer of the blood groups of races whose group percentages are unknown or imperfectly known. These studies are yielding results which may be expected to indicate something of the comparative value of the blood groups in studying the relationships of races. Results already obtained confirm the writer's belief that the so-called "biochemical index" of Hirschfeld and Hirschfeld is not a satisfactory criterion for studying this question. Too many authors have been willing to use the biochemical index as the main thing necessary to know about a race from the standpoint of its blood group characteristics. This is far from being the case, however, as can readily be shown. Two races, each having an equal proportion of agglutinogens A and B, and thus having the same "intermediate" index, might differ in that one had, for instance, 40% A and 40% B, with a small proportion of group I, while the other had only 3% A and 3% B, with a correspondingly large proportion of group I. In the first case, both agglutinogens are well-developed racial characteristics, while in the second case, neither is well developed. In both cases, however, the index would be the same. Likewise a race might have the factor A twice as abundant as B, its index thus placing it in Hirschfeld's "European" type, and yet if neither factor constituted a very large proportion of the total, this would be misleading.

The American Indians now being studied by the writer are an excellent example, their biochemical index putting them into the "European" type, but their very large proportion of group I being entirely different from typical European races. Any classification of races based on the blood groups must take these facts into account.

The question is a complicated one, and must be approached with extreme caution. Few if any pure races are now found, due to the endless migrations, displacements and interminglings to which mankind has been subject, together with the normal power of cross-fertility between all races. Moreover, it must be remembered that in general, racial characters are blending in inheritance, and are not sharply defined in succeeding generations. The blood group factors, however, being unit factors with complete dominance, are injected into a race "in toto," as it were, by crossing. They are there to stay. Consequently a little crossing, while not changing the obvious racial characters much, may modify to a noticeable extent the proportions of the groups. And while succeeding generations tend to cover up and blend the alien physical characters, the introduced agglutinogens retain their identity and become definite units in the hereditary complex of the race.

To throw light on the comparative value of the blood groups in solving this problem, it is desirable to examine compound races, made up of separate elements, each of whose blood group proportions is known. The study now being carried on by the writer on the group proportions of negroes, Indians and whites, and the hybrids of negro-white, negro-Indian, and Indian-white, is of such a nature.

The problem of the origin and relationships of races is not an easy one, and it is not certain that the blood groups will be able to play a very important part in its solution. The results so far obtained by independent investigators, however, when viewed together, seem to indicate that in general the blood group data conform remarkably well to the known anthropological facts. By approaching the problem with a clear understanding of its difficulties, bearing in mind the precautions outlined in this paper, a step may be gained by means of the blood groups towards the ultimate solution.

INDUCTANCE TREATED ACOUSTICALLY BY DIFFERENTIAL TELEPHONES

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Communicated May 21, 1925

1. *Introduction.*—The present note is a direct continuation of my last (these PROCEEDINGS, May, 1925). The two telephones in question actuate the ends of a brass tube, at the middle of which the nodal intensity is registered by a pin-hole probe and interferometer U-gauge. If a region of pulsating air communicates with still air by a pin-hole probe only, the stream lines are directed from the apex of the pin-hole cone to its base and their strength increases with the intensity of the node. If flow of air through the pin-hole is resisted, the corresponding pressure results.

In the graphs which follow s or Δs will denote the fringe displacement at the interferometer, proportional to nodal intensity under the conditions specified in detail. *Phase* refers to a vibration of the telephone plates simultaneously outward or inward. *Sequence*, to a vibration in which the plates are respectively outward and inward at the same time.

The adjustment of circuits is given in figure 1 (insert) where T and T' are the telephones, I a small inductor, E, the cell, B the break of controllable frequency. T' contains the auxiliary resistances R' and inductances L' and is reversible by the switch S.

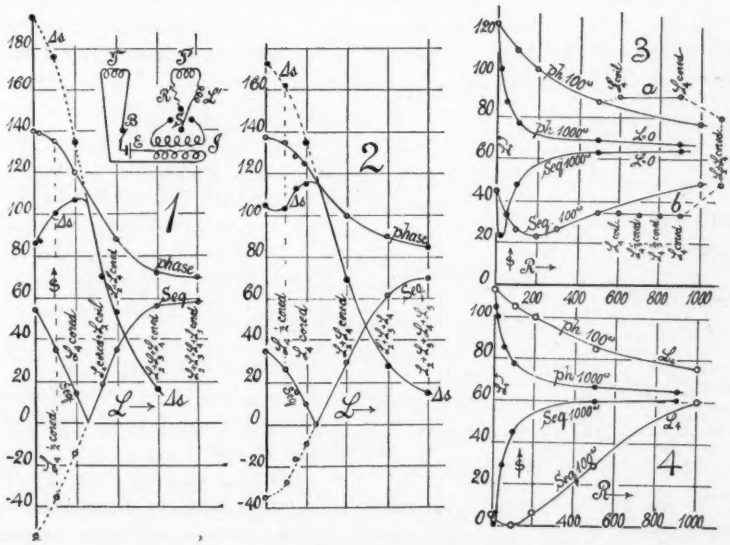
The two telephones in circuit lend themselves well for a variety of zero methods; but the interpretation of such results is troublesome and must here be omitted.

When the resistance and self-induction are small, the sensitivity of one or two fringes per millihenry increment is easily reached. This could be increased by selecting more sensitive pin-hole probes and virtually by using larger fringes. For convenience in observation, however, these should not be further apart than about $^1/_{10}$ millimeter on the ocular micrometer. Such fringes were used throughout the following work.

2. *Layers of Transformer in Parallel.*—To obtain greater initial currents for the sequence graphs, the two identical layers of the secondary of I, figure 1, were put in parallel. The telephone T is left in the primary. The surmise of improved detail is borne out in figure 1, where the fringe displacements s, are given in terms of the inductance L, increasing in steps. The experimental curve, $\Delta s = s_{ph} - s_{seq.}$, here shows a well marked maximum, while the sequence curve passes sharply through a minimum. By gradually inserting the iron core into the coil L_4, it was possible to trace these curves continuously; but unfortunately the minimum $s = 10$ was reached when the core was quite in. It is clear, however (cf. § 3), that the

sequence graph must actually fall to the abscissa and the curve is drawn to correspond.

If one considers the descending branch of the sequence curve negative in phase, the ascending branch positive as suggested by the dotted line, the doubly inflected curve resulting may be regarded as the true picture of the phenomenon, as a whole. Apart from the ends, the main part of the graph is now nearly straight. The same is true of the Δs graph, if the initial parts of the sequence graph are regarded negative in phase and therefore to be added to the phase graph. The Δs line is then surprisingly uniform in character with the characteristic double inflection.



The results in figure 1 deserve further elucidation to be obtained by changing the resistance of the T' circuit simultaneously. Figure 3 gives a case of the kind where R' only is increased (in steps of 100 ohms and of 1000 ohms, as stated) without further L' in the T' circuit. The new feature of the diagram is the minimum at about 200 ohms in the sequence graph, in the absence of additional inductance ($L' = 0$).

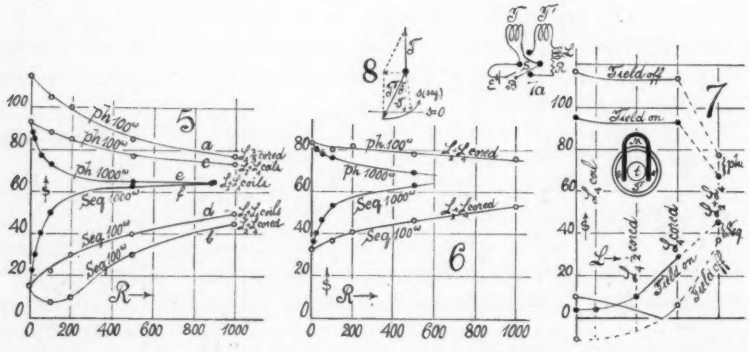
In figure 3, the branches a and b indicate the effects of increments of L' applied when $R' = 500$ ohms. There is little appreciable reduction of s and L becomes effective only when it is relatively large in value ($L_2 + L_4$).

In figure 4 the R-effect is investigated beginning with the additional inductance of the cored L_4 coil, in the T' circuit. Naturally the s values

as a whole are reduced and the R minimum of the sequence curve now actually falls to zero at $R = 100$ ohms. The sequence graph has been depressed and the minimum moved nearer the origin; whereas for high resistances the graph asymptotically reaches the precedent graph (Fig. 3 for $L = 0$).

In figure 5, R is increased in steps, beginning with an inductance smaller (coil L_4 with core $^2/_3$ in.; curves a, b) and larger (coils L_2 and L_4, not cored, curves c, d, e, f), respectively, than are impressed in figure 4, in which the origin is near the sequence minimum. Again the latter has been moved to the right and raised (curves a, b); or moved to the left beyond the coördinates (curves c, d, e, f) consistently with the preceding results.

Finally figure 6 gives the corresponding results when L_2 and L_4 (both cored) are inserted in the T' circuit. The coördinates as it were are further displaced to the right in the same sense as in figure 5.



To summarize the cases therefore: it is found that the s minimum of the sequence graph moves into smaller R and s toward the origin, when L is successively increased until the minimum vanishes. Thereafter the sequence graphs (without the minimum) rise again as L increases further; but this may in part be due to the R values of the new coils added in the later stages. The difficulty, not only of obtaining a sequence graph with an s-minimum when R varies (as compared with the preceding case of L-variation), but of bringing this minimum down to $s = 0$, is noteworthy. The next paragraph is a correlative illustration.

3. *Single Half Layer.*—Using but one of the identical layers of the inductor I, figure 1 (insert), fringe displacements s indicating the intensity of the middle node were obtained as summarized in figure 2. The decreased impedance as compared with layers in series is an advantage; but the high initial intensity or lead of the sequence curve of figure 1 (layers in parallel) has been lost because of the double resistance at the beginning.

By continuously inserting the iron cores, it was here possible to bring the sequence curve actually to and through $s = 0$, from which it follows that this must also have been the case in the preceding experiments, where the relevant data are incomplete. The dotted curves indicate the passage through zero where the phase opposition would be complete, when descending sequence branches are treated as negative in phase. They closely resemble figure 1 so that the remarks already made apply.

4. *Telephone Plate Subject to an External Magnetic Field.*—The question occurred whether in case of the adjustment without secondary Fig. 7*a* it would be possible to produce a lead in T' by magnetic attraction. In figure 7 (insert) T' shows the mouthpiece of the telephone, the bent magnet M being placed as near as possible to it, straddling the acoustic pipe t. The results given by the graphs in figure 7 are very definite. The vibration in phase is much diminished in strength, but is not otherwise abnormal. The sequence graph, however, is peculiar. The former lead at the beginning (field off), passing through zero with increased inductance, has practically vanished. Instead, the curve now rises continually and the divergence of curves is most marked when the sequence graph, in the absence of field, is at zero. This implies that the sequence vibration is also less intense, so that the graph as a whole rises higher throughout when the field is on. If the lead in the sequence graph (field off) is plotted negatively as shown by the dotted line, the initial similarity of the two sequence curves is evident.

If the magnet, M, figure 7 is reversed into the position from SN to NS its effect on s is similar, but only about half as large. At the opposed telephone T, the use of a second magnet gave only small differences. The effect observed is therefore here incidental, depending on the mounting of the plate of the telephone.

5. *Remarks.*—When a single telephone is active, the opposed plate functioning like a rigid wall, the nodal intensity s was found to be about $^2/_3$ of the intensity observed when both are vibrating in phase. Hence in so far as the fringe displacement s measures the nodal intensity, the vibrating plate in phase action contributes about as much intensity as the fixed plate reflecting.

In case of the adjustments figure 1 (insert), we may to a first degree of approximation consider the vibration vector of the unloaded telephone T, constant. In this case the vibration vector of the loaded telephone T' differs from it in magnitude and is set at a phase angle with regard to it, both of which vary with R and L in the above experiments. The magnitude eventually vanishes.

If we consult the usual diagram, of relations between the quantities $R, L, \theta = \tan^{-1} L\omega/R$, it appears that, on comparison with the corresponding change of the current I, θ increases most rapidly with L at constant

R, when L is small; similarly $\theta' = 90° - \theta$, in relation to I, increases most rapidly with R at constant L when R is small; for I under these circumstances is nearly normal (diametral) to the arcs of the corresponding circular loci of variation. We may therefore expect to find characteristic variations in the relations of θ and I at the beginning of the s-curves in the above graphs, as observed.

If in figure 8, T denotes the vibration vector of the unloaded telephone and T' the corresponding vibration vector of the loaded telephone at any instant, T' will be set at an angle to T. In the above work θ has appeared to be a lead, while T was apparently larger than T. Hence the fringe displacement will depend on the difference of T and the projection of T' on T in the sequence curves; and on their sum in the phase curves. The s-effect will not be simply additive, however, for the reasons given at the beginning of this paragraph. Moreover, the s-curves do not distinguish between sign changes of phase unless the curve branch is reversed as in figures 1, 2.

Hence if $T' > T$, we may have the s-curves passing through zero (minimum) in the sequence graphs by the simple shrinkage of T' with L or R, where T remains constant. The passage through zero here implied does not always occur.

If T' and T are nearly equal, we may have the sequence curves passing with increasing R through a minimum usually greater than zero, by the shrinkage of the angle θ, if it is taken as a T' lag and if $\cos\theta$ increases relatively more rapidly than T' decreases.

Finally, if θ beginning as a T' lead passes through zero into a lag with increasing L, while T' remains relatively stationary in value, the s-minimum should be much more strikingly reached and for $T' > T$ easily pass through zero, as has been observed throughout. Such a case is illustrated in figure 8, recalling that both an excess and a deficient T' produce a central node, the activity passing from one telephone to the other. Since the two last cases are mutually exclusive, whereas they seem to occur together, the complete explanation along these lines will require a further specification of data than is now available.

X-RAY RADIATION FROM HOT SPARKS

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Communicated May 29, 1925

Millikan has been able to study extreme ultra-violet spectra by using a high potential condensed discharge in a high vacuum as a source of light and specially ruled gratings, and he has found that many of the strongest spectrum lines are emitted by stripped atoms, that is, atoms with no valence electrons left. As these hot sparks also were found to radiate X-rays, the spectrum of which, however, has never been analyzed, the author undertook the problem of studying this spectrum, and this paper gives the first results.

In such a condensed discharge where the time during which the discharge takes place is a very small fraction of the total time, the current density during the instant of discharge is enormously high. For this reason an extraordinarily large proportion of the radiating atoms are *multiply ionized*, doubtless as a result of *successive impact*. If it is possible to remove an electron from the inner shells in such a stripped atom, we might expect that the X-radiation would be slightly different from the radiation emitted by a normal atom.

Another process of multiple ionization is that suggested by Wentzel[1] as an explanation of the so-called enhanced lines in X-ray spectra, and which involves the removal of more than one electron from the inner shells of the atom. In his first paper on this subject Wentzel supposed that this multiple ionization also was caused by successive impact, but later Rosseland[2] showed that this is extremely improbable, and that the simultaneous removal of two electrons by a single impact like that directly observed by Millikan[3] in the case of helium is much more probable. Coster,[4] furthermore, in his experiment was unable to get the enhanced line $L\alpha_4$ for silver at a voltage of 4700 volts, although the critical potential for the L-series of silver is only about 3350 volts. Siegbahn also has found an absorption edge for sulphur at a wave-length corresponding to about the double critical voltage of the K-series. All these facts seem to indicate that the atom is *multiply ionized* by a *single impact*. On the other hand Bäcklin[5] has recently been able to photograph the line $K\alpha_4$ for aluminum at a voltage lower than that required for the removal of both K-electrons by a single impact.

In the case of successive ionization as applied to the inner shells we should expect, as has been pointed out by Wentzel, that the relative intensity of the enhanced lines and the ordinary lines corresponding to them would increase with the second power of the current density. In a con-

densed discharge we should expect on this account a very great increase in this relative intensity, but in the case of multiple ionization by a single impact we might expect the same intensity as is observed with an ordinary X-ray tube.

The vacuum spectrograph which was used is one of Siegbahn's type, and has been described by him.[6] Instead of the X-ray tube a spark chamber of the construction shown in figure 1 was connected with the spectrograph.

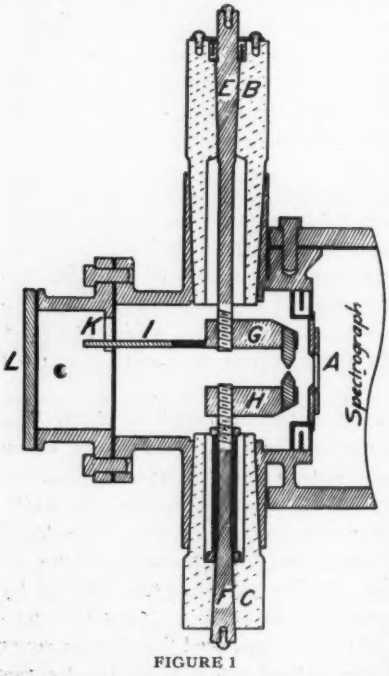

FIGURE 1

The chamber is made of a brass tube about three inches in diameter the end of which carries the slit A. The tube is soldered in the wall of the spectrograph in such a way that the slit and the photographic plate in the spectrograph are on the same distance from the rotating axis of the crystal (focus condition). B and C are two conical grindings made of bakelite, and in each of them is another grinding, E and F, of brass. These serve as holders for the two metal pieces, G and H, in which the electrodes are fastened. In order to obtain a more concentrated spark the electrodes are pointed. The distance between the spark and the slit is about 1 cm. The upper electrode holder G is threaded on the rod E, and by turning this rod at the upper end the distance between the electrodes can be regulated from outside. The electrode holder is prevented from turning by means of a glass rod, I, and a fork, K, fastened on the wall of the chamber. The spark can be observed through the glass window, L. The spark chamber and the spectrograph are connected through a series of holes, shown in the figure, and thus both compartments can be evacuated to the same high vacuum through a tube in the side of the spark chamber by means of mercury condensation pumps.

The electrodes E and F are arranged in series with another outside spark gap, provided for the purpose of controlling the energy in the vacuum spark. The two spark gaps, shunted by a capacity of four Leyden jars, were connected across the secondary of a Thordarson wireless transformer of 1 K.V.A. capacity at 25,000 mean volts. On account of the production of

excessive heat the spark was run intermittently so that the actual time of sparking was about one sixth of the total time.

The slit must be covered with a filter which absorbs the visible light but is as transparent as possible for the X-rays. As the atomic absorption increases approximately as the fourth power of the atomic number—provided one is not working with wave-lengths longer than the K absorption edge—it is evident that the filter ought to be composed of elements of low atomic number. I used as filter a thin film of celluloid, which was obtained by letting a drop of celluloid-solution in amyl-acetate fall on water, and which was rendered opaque by means of a thin coat of India ink. Such a film was found more transparent for soft X-rays than filters of aluminum (7μ), colored goldbeaters skin, and carbon paper, ordinarily used.

I tried silver, aluminum, silicon, sulphur and copper as electrodes, and used a gypsum crystal as grating. *The plates which were obtained show beautifully all the earlier known characteristic lines in the spectrum of the L-series for silver, and the K-series for the other elements, including the so-called spark-lines, but no new lines could be observed, nor could one notice any shift or broadening in the old ones.* This result indicates that the X-rays obtained are not produced by the stripped atoms in the vapor. In order to find out from what region of the spark the X-rays originate, I used as electrodes two pieces of aluminum sheet, and arranged them with their edges parallel to the slit. On the other side of the slit I placed a photographic plate and secured in this way a picture of the spark as through a pinhole camera. The result of this test is shown in Fig. 2. The picture indicates definitely that the X-rays to a very great extent originate at the solid electrodes, and that the X-radiation from the vapor in the spark itself, where we have stripped atoms, is practically negligible.

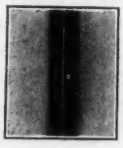

FIGURE 2

The relative intensity of the lines also was, as far as could be judged by looking at the plates, the same as that obtained from an ordinary X-ray tube. *This fact shows rather definitely that the multiple ionization giving rise to the enhanced X-ray lines of the K-series must be due to simultaneous ejection by a single impact.*

The work is being continued, and by rearranging the apparatus in order to get much more energy in the spark, I hope to be able to get X-radiation from the vapor.

[1] G. Wentzel, *Ann. d. Phys.*, **66**, 437 (1921); and **73**, 647 (1924).
[2] S. Rosseland, *Phil. Mag.*, **45**, 65 (1923).
[3] R. A. Millikan, *Phys. Rev.*, **18**, 456 (1921).
[4] D. Coster, *Phil. Mag.*, **44**, 546 (1922).
[5] E. Bäcklin, *Zeits. f. Phys.*, **27**, 30 (1924).
[6] M. Siegbahn, *Spektroskopie der Röntgenstrahlen*, Berlin, 1924.

THE FOUR TRANSVERSE EFFECTS AND THEIR RELATIONS IN CERTAIN METALS

BY EDWIN H. HALL

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Read before the Academy April 27, 1925, and subsequently broadened

There have been many theoretical discussions of the Hall effect. Some of these have made much of the fact that in certain crystals conductivity, both thermal and electric, is known to be "æolotropic," different in different directions, and have explained or, rather, described, the effect in question as due to æolotropy set up by action of the magnetic field. Others have made prominent the direct "ponderomotive" action of the magnetic field on elements of the electric current, the moving electrons or ions.

I have long been of the opinion that, in some metals at least, the Hall effect is not to be explained by this ponderomotive action alone, even if more than one mode of electric conduction is admitted. Thus, the rotation of the equipotential lines of the electric current by action of the magnetic field is about one hundred times as great in bismuth as in gold. In tellurium it is perhaps greater than in bismuth but in the opposite direction. It seems unlikely that the very large effects, of opposite sign, in bismuth and tellurium, respectively, can be explained without recourse to conductive æolotropy produced or modified by the action of the magnetic field.

Until recently, however, I have had a hope that the small Hall effects, of negative sign, observed in certain metals, aluminium, copper, gold, silver, palladium and platinum, could be satisfactorily accounted for by the hypothesis of direct action on the electric current itself, this current having the dual character which my writings have so frequently described. In this hope I wrote a paper[1] which was read at the November, 1922, meeting of the National Academy. In that paper I undertook to state the relations of the four transverse effects to each other in terms derived directly from my theory of electric and thermal conduction, and in particular to calculate from the observed values of the Hall and Ettingshausen coefficients in certain metals values of the Nernst and the Righi-Leduc coefficients for the same metals. For brevity, however, I left out the very complicated formula which I had obtained for the relation of the Nernst effect to the Hall effect, giving merely numerical results derived by application of this formula.

In a paper presented in April, 1924, to the Solvay Conference in Brussels I continued the effort described and gave at great length the derivation and application of the formula in question, using data which I had obtained from my own recent experiments on gold. It thus appeared that, while I could deal more or less satisfactorily with the problem in hand so long as

I kept to the data of a single temperature, serious difficulty was met when the data obtained at different temperatures were compared. I have more recently had a like experience with palladium, in which I have, within the last year, measured all four of the transverse effects at various temperatures. Close examination of the situation leads me to the conclusion that my main trouble lies in the assumption, on which I have been working, that the Hall effect, so far as it is dependent on the free-electron stream crossing the magnetic field, can be calculated from the simple ponderomotive force exerted on it by the field. I am now strongly inclined to the opinion that the action in question is, even for such metals as gold and copper, more complicated than the assumption just stated would make it, and that in some metals the free-electron stream may even contribute to the formation of a positive Hall effect. Apparently it does so in cobalt, iron and zinc.

I have as yet no theory sufficiently definite to be formulated as to how this action can occur, though it seems probable, as Mr. Eldridge has suggested,[2] that its explanation may ultimately be found in a study of space lattice conditions within the various metals.

This does not mean, however, that I have given up the idea of applying to the transverse effects the conceptions of my dual theory of electric and thermal conduction. I still feel that these conceptions are useful, if not absolutely essential, in giving a physical picture to supplement the thermodynamic relations which Bridgman[3] has worked out between the four transverse effects. I shall presently in this paper undertake to develop this picture, but with a broader conception of the Hall effect than the one I have in my previous writings employed. As a preliminary I will give the results of my experimental work of the past two years on the four transverse effects in four different metals, all the effects for any one metal having been measured in the same piece. I must leave to be given in a later paper details of the experiments in question. All were made with a field strength of about 9000–9500 gauss.

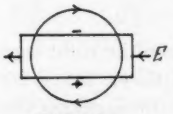

FIGURE 1
Hall effect,
R or ${}_eT_e$,
positive.

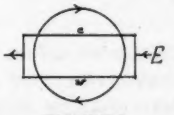

FIGURE 2
Ettingshausen effect,
P or ${}_eT_h$,
positive.

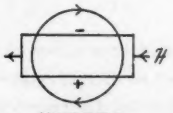

FIGURE 3
Nernst effect,
Q or ${}_hT_e$,
positive.

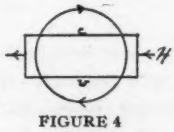

FIGURE 4
Leduc effect,
S or ${}_hT_h$,
positive.

Figures 1–4 will serve to describe the four transverse effects under discussion and to show the sign conventions that are commonly used in dealing with them.

The results referred to above are contained in Table I. All the values there given may be, as to absolute magnitude, affected by errors of several per cent, and those of P and S, which depend on slight differences of temperature difficult to measure, by errors of many per cent. Especially great percentage uncertainty attaches to the values of P in gold. The relative values of any one coefficient at different temperatures in the same metal are doubtless more accurate than the absolute values.

TABLE I

VALUES OF R, P, Q AND S IN CERTAIN METALS

METAL	TEMP.	$R \times 10^8$	$P \times 10^9$	TEMP.	$Q \times 10^8$	$S \times 10^9$
Gold	17°	−705	−1.2	25°	−181	−300
	72°	−696	−0.4	57°	−181	−263
Palladium	26°	−845	+17.4	25°	+327	−48.7
	45°	−855	+19.1	45°	+326	−41.4
	64°	−844	+22.2	67°	+335	−37.8
Nickel	22°	−4520	+60.6	38°	+2590	−528
	57°	−5910	+105.7	57°	+3040	−494
	86°	−7280	+154.2	77°	+3660	−447
Cobalt	19°	+3550	+81.0	25°	+1900	+377
	48°	+4440	+109.0	47°	+2190	+429

Table II shows the results of my attempt to calculate values of Q and S from observed values of R and P, in case of gold and palladium, by use of the method, indicated above, employed in my paper of February, 1923, and in equations preceding equation (109) in my Solvay Conference paper (not yet published).

TABLE II

METAL	TEMP.	$R \times 10^8$ OBS.	$P \times 10^9$ OBS.	$Q \times 10^8$ CALC.	$Q \times 10^8$ OBS.	$S \times 10^9$ CALC.	$S \times 10^9$ OBS.
Gold	25°	−704	−1.05	−490	−181	−192	−300
	55°	−699	0.62	−300	−181	−205	−264
Palladium	25°	−844	+17.3	+243	+327	−122	−48.7
	45°	−855	+19.1	+269	+326	−122	−41.4
	65°	−843	+22.5	+314	+334	−125	−38.0

It is to be observed that all of the calculated values have the right sign and the right order of magnitude. Indeed, any one of them, taken by itself, might, in view of the uncertainty of some data entering into the calculations, be regarded as encouraging, if not distinctly satisfactory. The serious difficulty to which I have alluded lies farther back. If I continue to write for R_f, the Hall coefficient which the free-electron stream, alone, would give, the simple expression

$$R_f = \frac{-6.28l}{k\ T^{0.5}}, \qquad (1)$$

which represents the direct influence of the ponderomotive force on this stream, I find that the value of l (the "mean free path" of the electrons), as derived from the observed values of R and P, does not vary with temperature as my theory of electric and thermal conduction requires it to vary. Now, to be sure, I might give up this theory, but in doing so I should have to give up my attempt to present a physical picture showing the mutual relations of the four transverse effects, and this attempt is still too promising to be abandoned. So I prefer to give up equation (1), as a complete expression for R_f in any metal, and assume that some condition, at present obscure, possibly dissymmetry of electric conduction, set up or modified by the magnetic field acting on the current-bearing metal, has a large part, perhaps the main part, in producing the Hall effect.

Defining R_f merely as the Hall coefficient which the free-electron stream, alone, would give, and R_a as the Hall coefficient which the associated-electron current, alone, would give, I shall, on the ground given in my paper of February, 1923, already referred to, write here eq. (7) of that paper as

$$R = (R_a k_a + R_f k_f) \div k, \qquad (2)$$

where k is the total electric conductivity of the metal, k_a that due to the associated electrons, and k_f that due to the free electrons.

Other equations reproduced from the same paper I shall mark in [ ] with the numbers they have in that paper. The next one is

$$P = (R-R_f)\, k_f(\lambda \div \theta) = (R-R_f)\, k_f \div I', \qquad (3) \quad [8]$$

in which P is the Ettingshausen coefficient. In place of $(\theta \div \lambda)$, defined in my previous paper already referred to, I now put its equivalent I', defined as the strength of the cyclic electric current which, according to my view of thermal conduction, flows in a bar of metal of unit cross-section having unit temperature gradient. Values of k, k_a, k_f, and I' can be found in, or derived from data given in, my "*Summary*,"[4] and so, when values of R and P are known from experiment, the values of R_a and R_f can be found by use of equations (2) and (3).

The next step is to find an expression for Q in terms of R_a and R_f. It is just here that, in my previous attempts, I have gone through a very laborious process of reasoning, making use of the now partially abandoned conception embodied in equation (1), leading to a long and rather complicated formula. I still think that this formula, or something very like it, would have its part to play in a thorough-going discussion of the relations between R_f and Q; but, as I cannot at present evaluate the different parts of R_f, I must now take a different course, one which, though not claiming complete accuracy, has the very great merit of brevity and comparative clearness.

Let us suppose that we have an electrically isolated metal bar of square cross-section, 1 sq. cm. in area, extending across a field of strength H and having within it a temperature gradient g. According to my views, an associated-electron current of strength gI' will be running up this temperature gradient, and an equal free-electron current will be running down the temperature gradient. The up-grade current, acting alone, would give a Nernst coefficient Q_a, the sign of which would, according to the usual convention, be the same as the sign of R_a in the Hall effect. If δ_a stands for the transverse potential gradient due to this current, we have by definition

$$Q_a = \delta_a \div gH. \tag{4}$$

But δ_a may be regarded as due to a Hall effect on the up-grade associated-electron current gI', which under ordinary Hall effect conditions would imply a total electric current of strength equal to $gI'(k \div k_a)$. And so we can write

$$\delta_a = R_a H gI'(k \div k_a). \tag{5}$$

From eqs. (4) and (5) we get

$$Q_a = R_a I'(k \div k_a) \tag{6}$$

Similarly, but with a change of sign due to the fact that the free-electron stream runs in the same direction as the heat flow, we have

$$Q_f = -R_f I'(k \div k_f). \tag{7}$$

Analogous to eq. (2) we have

$$Q = (Q_a k_a + Q_f k_f) \div k. \tag{8}$$ [10]

From eqs. (6), (7), and (8) we have

$$Q = (R_a - R_f)I'. \tag{9}$$

The step from the Nernst effect to the Righi-Leduc effect is by way of the equation

$$S = (Q - Q_f) k_f(\lambda \div \theta) = (Q - Q_f) k_f \div I', \tag{10}$$ [12]

which is strictly analogous to eq. (3).

By means of eqs. (2)–(10) we can go easily from the observed values of R and P to calculated values of Q and S. The results of this process, applied not only to gold and palladium but to every metal for which I have the necessary data, are shown in Table III. The letters following the names of the metals indicate the names of the investigators who have given the *observed* values of R, P, Q and S. Thus, U is for Unwin,[5] H for Hall (see Table I), $H\&C$ for Hall and Campbell,[6] and Z for Zahn.[7] The

value of H was about 4000 in the experiments of Zahn, about 5000 in those of Hall and Campbell, usually something over 9000 in those of Hall alone, and is not definitely stated for the work of Unwin. The table contains every combination of algebraic signs that is known to exist among the transverse coefficients.

It is to be noted that in all cases the calculated values have the right sign and, in all cases except that of S for bismuth, a proverbially inconstant material, the right order of magnitude. It should be remembered that in every case data necessary for the calculation were taken from tables given in my *Summary*, tables based largely on information furnished in Bridgman's papers describing experiments on metals in wire form, different specimens in every case from those used in the transverse effect observations referred to. In the case of cobalt, a difficult metal to work with, the calculated value of S is greater than the observed value in the specimen

TABLE III

METAL	TEMP.	$R \times 10^4$ OBS.	$P \times 10^9$ OBS.	$Q \times 10^4$ CALC.	$Q \times 10^4$ OBS.	$S \times 10^9$ CALC.	$S \times 10^9$ OBS.
Copper	*U* 18°	−4.7	−1.4	−1.8	−1.9	−240	−210
Gold	*H* 25°	−7.04	−1.1	−0.97	−1.81	−291	−300
	H 55°	−6.99	−0.6	−0.50	−1.81	−270	−264
Silver	*U* 18°	−5.1	−1.0	−1.4	−1.8	−290	−270
Alumin.	*U* 18°	−2.8	+0.79	+0.45	+0.42	−110	−62
Bismuth	*Z* 18°	−63300	+35300	+560	+1780	−61000	−2050
Nickel	*H* 37.5°	−51.0	+79.2	+14.5	+24.8	−601	−528
	H 57.5°	−59.3	+107	+18.4	+29.2	−685	−493
	H 77.5°	−68.3	+142	+22.9	+35.2	−770	−446
	U 18°	−38.6	+40	+7.4	+10.0	−440	−250
Pallad.	*H* 25°	−8.44	+17.3	+3.89	+3.27	−153	−48.7
	H 45°	−8.55	+19.1	+4.15	+3.26	−153	−41.4
	H 65°	−8.43	+22.5	+4.78	+3.34	−157	−38.0
Iron *H. & C.*	13°	+79.4	−49.3	−11.1	−8.6 at 31°	+1000	+560 at 51°
	U 18°	+87	−43	−9.9	−9.5	+980	+520
Zinc	*U* 18°	+7.2	−2.5	−1.65	−0.73	+143	+110
Cobalt	*H* 25°	+37.2	+87	+19.5	+19.0	+84	+376
	H 45°	+43.4	+106	+22.7	+21.7	+82	+425
	U 18°	+26	+23	+5.2	+7.8	+178	+110

used by Unwin and less than the observed value in the specimen used by myself. I suspect, as I have already indicated, large percentage inaccuracy in my observed values of P for gold, as this quantity is small and my apparatus was not in good condition when it was measured. If I were to take P at 25° as 1.5 times the value I have used, the calculated value of Q would be —0.000147 instead of —0.000097, thus giving much better agreement with the observed value, —0.000181, while the calculated value

of S would be affected but little, becoming -278×10^{-9} instead of -291×10^{-9}.

On the whole, it appears that the concrete physical theory of electric and thermal conductivity which I have been putting forward during the past few years, whatever may be thought of its fundamental soundness, enables us to explain the qualitative relations of the four transverse effects and to calculate, with an approach to accuracy, the values of the thermomagnetic coefficients Q and S from the observed values of the electromagnetic coefficients R and P.

[1] *Proc. Nat. Acad. Sci.*, Vol. 9, No. 2, Feb., 1923.

[2] *Phys. Rev.*, 2nd series, Vol. 21, No. 2, Feb., 1923, p. 131.

[3] *Phys. Rev.*, Vol. 24, No. 6, Dec., 1924, p. 644. Bridgman's argument may need some restatement, in view of the fact that the Moreau equation, $Q = \sigma R/\rho$, which this argument accepts, has members of opposite sign in the case of cobalt.

[4] *Proc. Nat. Acad. Sci.*, Vol. 7, No. 3, March, 1921.

[5] *Proc. Roy. Soc. of Edin.*, **34**, 1913–14, p. 208, and **41**, 1920–21, p. 44.

[6] *Proc. Amer. Acad. Arts Sci., Boston*, **46**, p. 625, 1911.

[7] See Campbell's *Galvanometric and Thermomagnetic Effects*, Monographs on Physics, Longmans.

THE DISTRIBUTION OF ENERGY IN THERMAL RADIATION AND THE LAW OF ENTIRE EQUILIBRIUM

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The law of entire equilibrium, which I advanced in a recent number of these Proceedings,[1] has been, in a less general form, in the minds of a number of scientists. Boltzmann's assumption that a gas is "molekular ungeordnet" is a special case under this law. Several approaches to the completely general principle are quoted in recent articles by Fowler,[2] Milne,[3] and Dirac,[4] who have applied to a number of important equilibria a principle analogous to the one that I proposed. Both Mr. Fowler[5] and Mr. Tolman[6] have been kind enough to inform me that they are publishing notes referring to a number of previous statements of principles similar to the law of entire equilibrium, and with which I greatly regret that I was unfamiliar when I published the preceding article.

Several of the statements quoted in these papers appear at first sight as general as my own, but there have always been certain reservations, explicit or implicit, and the very most that has been suggested by other authors can be comprised in the following statement. In a condition of thermal equilibrium, if certain atoms or sets of atoms in a state L pass into

a state Q, through any number of intermediate states, M, N ..., then in an equal time equal numbers of atoms (or sets of atoms) will pass from the state Q to the state L, and through precisely the same intermediate states.

However, this statement by no means comprises the full content of the law of entire equilibrium, for in a complete description of a physicochemical process we must include many things besides the energy states of the several atoms. For example, we must describe the energy of various static fields, and especially the conditions of radiant energy within the system.

The full application of the law of entire equilibrium to radiant energy seems to me a crucial test of its validity, and since by this application we are going to be led to conclusions of a quite unorthodox character, many will doubtless prefer to deny the law of entire equilibrium rather than abandon many of the accepted laws of radiant energy. But I believe that the law of entire equilibrium will ultimately be recognized as one of the most fundamental of natural laws, and that whatever consequences may be drawn from it must be accepted, even though they contradict well established beliefs.

The Planck Distribution Law.—If we accept the law of entire equilibrium and apply it to the emission and absorption of light, we are led at once to important conclusions. If we should assume that an atom in equilibrium with radiant energy emits radiation in the form of a series of spherical waves receding from the atom, then we should be obliged to assume that the same atom absorbs energy from a similar series of concentric waves converging toward the atom. This is a picture which does not accord with any existing theory of light. (Such a picture might conceivably be interpreted if we should postulate negative energy.) Again, if we assume that light is emitted by atoms in single abrupt processes, then we must conclude that light is absorbed by the same atoms in single abrupt processes, and I believe that it was this kind of consideration that originally led Einstein to advance the modern corpuscular theory of light.

It is immediately evident from such considerations that the method of deriving Planck's distribution formula, which was preferred by its author, and which assumes that atoms absorb light in a continuous manner but emit light in quanta, is quite incompatible with the law of entire equilibrium.

Let us turn next to the well known derivation of the Planck distribution formula which has been given by Einstein.[7] He considers a kind of atom which may exist in certain discrete energy states such as Z_m, Z_n, with corresponding internal energies ϵ_m, ϵ_n, and for the fraction of molecules existing in a single state Z_n he writes

$$W_m = p_m e^{-\epsilon_m/kT}; \; W_n = p_n e^{-\epsilon_n/kT}. \qquad (1)$$

Each p is a constant characteristic of the state. When these atoms are in thermal equilibrium with radiant energy he assumes that in unit time the number of atoms leaving state Z_m for the state Z_n is equal to the number leaving the state Z_n for the state Z_m. In other words, he tacitly eliminates the possibility of a cyclic equilibrium whereby Z_m could pass predominantly to Z_n, Z_n to Z_l and Z_l to Z_m. So far therefore his assumptions are in complete accord with the law of entire equilibrium.

Einstein next considers radiant energy of such frequency that $h\nu = \epsilon_m - \epsilon_n$. The density of such energy may be designated as u_ν (departing slightly from his notation). The rate of formation of Z_m from Z_n he writes proportional to the fraction of atoms in the state Z_n and to u_ν, while the rate of spontaneous fall from Z_m to Z_n, with the evolution of light of frequency ν, he writes proportional to the fraction of atoms in the state Z_m. Thus if s_{nm} and s_{mn} are the two rates, we may write

$$s_{nm} = B_n^m W_n u_\nu; \quad s_{mn} = A_m^n W_m \tag{2}$$

for the two processes which may be represented schematically as

$$Z_n + h\nu \longrightarrow Z_m \qquad (a)$$
$$Z_m \longrightarrow Z_n + h\nu. \qquad (b)$$

Of these two processes one is simply the reverse of the other, and by the law of entire equilibrium we must therefore equate the two rates, thus obtaining from (1) and (2),

$$u_\nu = \frac{A_m^n p_m}{B_n^m p_n} e^{-h\nu/kT}. \tag{3}$$

But this is the form of the distribution equation of Wien.

In order to obtain the Planck formula, Einstein made the further assumption that in addition to the spontaneous change of the state Z_m to the state Z_n, this process is stimulated by the presence of light of the frequency ν. This additional process may be represented schematically as

$$Z_m + h\nu \longrightarrow Z_n + 2h\nu. \qquad (c)$$

Now there is no objection to this assumption. In fact it seems probable that the rate of fall from Z_m to Z_n will depend not only upon the presence of radiant energy of frequency ν, but also upon the presence of light of all frequencies.

But Einstein now equates the rate of (a) to the sum of the rates (b) and (c), which absolutely contradicts the law of entire equilibrium, according to which the process (c) would be just balanced by the process (d), namely,

$$Z_n + 2h\nu \longrightarrow Z_m + h\nu. \qquad (d)$$

The existence of processes (*c*) and (*d*) in no way influences the rates (*a*) and (*b*). The great power of the law of entire equilibrium lies in the fact that a process may be divided into many detailed processes, and that an independent equation is obtained by equating the rate of *each* detailed process to the rate of the inverse process.

Thus our law leads directly to a formula which is of the form of the Wien and not of the Planck equation. But the former equation is known to be contradicted by experiment, while the latter has been verified within narrow limits of error. At first, therefore, it would seem that this crucial test of the law of entire equilibrium demonstrates its invalidity. Let us not make this judgment too hastily.

The fact is that Equation 2 involves a number of assumptions that can only be justified under certain ideal circumstances. I shall not speak here of the logical difficulties involved in the supposition that the states Z_m and Z_n correspond to exact energy contents ϵ_m and ϵ_n, and therefore that the light causing the change from Z_n to Z_m must be strictly monochromatic, but I shall question the assumption that the rate of a process is proportional to the concentrations of the entities which are responsible for this process.

It is well known in chemical thermodynamics that except in ideal cases the equilibrium between substances is determined not by their concentration but by a thermodynamically corrected concentration which I have called the *activity*. Moreover, since the state of equilibrium is fixed by the relative rates of a number of processes, these rates are also determined not by concentrations but by activities. The concept of activity has hitherto been applied only to chemical substances, but there is no reason why it should not be applied to any entity which enters into a physicochemical process. Let us represent by a_m and a_n the activity of the atoms in the states Z_m and Z_n, and by a_ν the activity of light of frequency ν, and let us write for the rates of the processes (*a*) and (*b*), at equilibrium,

$$s_{nm} = \mathbf{K}_{nm} a_n a_\nu = s_{mn} = \mathbf{K}_{mn} a_m. \tag{4}$$

Now while Equations 1 are not thermodynamically correct as given, they are correct (in this simple case) if we use the activities, and thus we have

$$a_m/a_n = pe^{-h\nu/kT}, \tag{5}$$

and therefore by (4)

$$a_\nu = \mathbf{K}_{mn}/\mathbf{K}_{nm} pe^{-h\nu/kT}. \tag{6}$$

The constants $\mathbf{K}_{mn}$, $\mathbf{K}_{nm}$ and p are independent of the temperature, but they may depend upon the particular energy states chosen, and therefore upon the frequency ν, so that we may write

$$a_\nu = f(\nu)e^{-h\nu/kT}. \tag{7}$$

Let us define a_ν more precisely. If u is the density of total radiant energy, and $u_\nu = \partial u/\partial\nu$ is the density of radiation lying between the frequencies ν and $\nu + \partial_\nu$ we may define two new quantities, ρ and ρ_ν, by the equations,

$$\rho_\nu = \partial\rho/\partial\nu = u_\nu/h\nu, \tag{8}$$

so that if at any time we desire to use the corpuscular theory, ρ and ρ_ν will represent, respectively, the total number of light quanta, and the number of quanta of the specified type, per unit volume.

We shall now define the activity of radiation just as we define the activity of a chemical substance. Thus a_ν will have the dimensions of ρ_ν, and will approach ρ_ν in a given space when the concentration both of matter and of radiant energy in this space approaches zero.

We may write Wien's equation as

$$\rho_\nu = 8\pi/c^3 . \nu^2 e^{-h\nu/kT}. \tag{9}$$

and may regard this equation as a true limiting law, but, as a general equation for the distribution of thermal energy, we must now write

$$a_\nu = 8\pi/c^3 . \nu^2 e^{-h\nu/kT}. \tag{10}$$

The Laws of Ideal Radiation.—If we consider the distribution of quanta among the different frequencies as analogous to the distribution of the molecules of a gas between different kinetic energies, it has often been observed that the kind of reasoning which leads to the Maxwell distribution formula seems to lead directly to the Wien distribution, and only by assumptions of an unusual character can the Planck equation be obtained. It is particularly interesting to consider the generalized form of the Maxwell equation obtained from relativity by Jüttner,[8] Tolman,[9] and later by Dr. Adams and myself.[10] This equation when the mass of the molecules is very small or their velocity is very large, assumes the form

$$\frac{\partial N}{\partial E} = \frac{N}{2k^3T^3} E^2 e^{-E/kT} \tag{11}$$

where N is the number of molecules (let us say in unit volume) and E is the energy of a single molecule. Now if we replace N by ρ, and E by $h\nu$, Equations 9 and 11 become identical, even to the specific constants (as may readily be seen by integrating Equation 9 and thus obtaining the value of ρ).

All this, however, is analogy and not proof, but this would cease to be the case if we could assume that light may interact with light without the intervention of molecules, for then by precisely the same methods as lead to Equation 11 we could obtain a direct derivation of the Wien equation. But are we not obliged to assume that light does interact with light? Even

if we should assume no other interaction, would not the theory of gravitation force us to believe that one quantity of light must act upon another since they are both quantities of energy and therefore of mass? If such interaction is granted then we have a proof of the Wien equation which is just as valid as the proof of the Maxwell equation.

Once more we face the objection that Wien's equation is untrue, but so in fact is Maxwell's. The latter equation is true not for an actual but for an ideal gas, and if we examine the point in the derivation which results in this limitation we find that it is the assumption that the molecules of a gas are so far apart that the time during which molecules are in contact is negligible compared to the time when they are apart. When a similar assumption can be made regarding light quanta we can justify the Wien equation, and only then.

In another connection Dr. Smith and I,[11] in considering the interaction between molecules and light, have concluded that the "radius of action" of a quantum is greater, the smaller the frequency. We may similarly consider that two light quanta have a greater mutual influence the smaller their frequencies. In other words, we are led to conclude that we can speak of ideal radiation in the same sense that we speak of an ideal gas, and that the exact distribution equation for ideal radiation is the Wien equation. The deviations from the ideal state and from the Wien equation will be greater the greater the concentration of quanta and the smaller their frequency. That is, the deviations from the Wien equation will increase with increasing values of T/ν, as is found by experiment.

Let us suppose that the interaction between two light quanta is manifested by a temporary slowing up of each quantum, so that in a space containing a high concentration of light the average velocity of light is less than that in free space. Then it will no longer be strictly true that the pressure of radiation upon the walls of an enclosure is equal to one-third of the density of the radiation.

However, this proportionality is assumed in the thermodynamic derivation of Stefan's law and Wien's displacement law, both of which have been regarded hitherto as purely thermodynamic, but now must be considered only as true limiting laws for ideal radiation but not quite exact for actual radiation. As a corollary it may be pointed out that any equation like Planck's which conforms to Stefan's law and Wien's displacement law, cannot represent actual radiation.

These are a few of the startling consequences of the law of entire equilibrium. In this preliminary note I can do no more than show the general character of the modifications in existing belief which the adoption of this law will require. Lest, however, it seem that the results of this investigation are too largely destructive in character, I shall restate, in a different form, the one positive result of the discussion, namely, that in a system of

radiation in thermal equilibrium the activity of the radiation follows exactly the Wien distribution formula.

Let us consider a hohlraum with a number of windows, each of which is capable of transmitting only some very narrow band of the spectrum. Each of these windows communicates with a separate enclosure, empty and with reflecting walls. Soon after thermal equilibrium is established in the central hohlraum the side enclosures will contain a constant very small concentration of nearly monochromatic light. The theorem which results from the present discussion is that the concentrations of the several frequencies of light in the several enclosures will not be the concentrations which prevail in the main hohlraum, but will be precisely the concentrations given by the Wien distribution formula.

[1] Lewis, *Proc. Nat. Acad. Sci.*, **11**, 179 (1925).
[2] Fowler, *Proc. Cambridge Phil. Soc.*, **22**, 253 (1924).
[3] Milne, *Phil. Mag.*, **47**, 209 (1924).
[4] Dirac, *Proc. Roy. Soc.*, **A 106**, 581 (1924).
[5] Fowler and Milne, these PROCEEDINGS, **11**, 400 (1925).
[6] Tolman, *Ibid.*, **11**, 436 (1925).
[7] Einstein, *Physik. Zs.*, **18**, 121 (1917).
[8] Jüttner, *Ann. Physic.*, **34**, 856 (1911).
[9] Tolman, *Phil. Mag.*, **28**, 583 (1914).
[10] Lewis and Adams, *Physic. Rev.*, **5**, 510 (1915).
[11] Lewis and Smith, *J. Amer. Chem. Soc.*, June, 1915.

IONIC MOBILITIES IN ETHER AS A FUNCTION OF PRESSURE

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Introduction.—In 1922 Erikson[1] using a gas blast method measured ionic mobilities in air at different velocities of the gas. He found that while the negative ions have a single constant mobility (about 1.8 cm./sec.), the positive ions when first formed have the same mobility as the negative ions but that in about 0.004 second after formation their mobility drops to a lower value (about 1.4 cm./sec. the commonly accepted value of the positive ion mobility in air). These results have since been extended to N_2, O_2, CO_2 ions, and to hot Pt and Ac A and B ions in air by Erikson.[2,3,4] Wahlin[5] repeated Erikson's measurements in air using the Franck modification of the Rutherford alternating current method. He varied the age of his ions by changing the auxiliary field applied to the ions to drive them through the gauze. Wahlin[6] has recently extended his measurements to He with similar results. Although Wahlin's results confirm

those of Erikson their value as a confirmation might be questioned because of secondary effects produced by changing the auxiliary field. It might be added that results similar to Erikson's had long ago been observed by Todd[7] using an alternating current method. At that time they however received a different interpretation.

Statement of Problem.—All these experiments definitely tend to show that newly formed positive ions have higher mobilities than the positive ions a few hundredths of a second old. They furthermore show that when the negative ions of the species can be studied the value of the mobility of the newly formed positive ion equals that of the negative ion. The interpretation of the results is at present very obscure as will be seen from the discussion at the end of the paper. Further experimental knowledge of the facts seems essential. To obtain further information the writer felt it of interest to study the behavior of the positive ions in a class of gases hitherto not studied in this regard: to wit those in which the positive and negative ions apparently have the same mobilities. While in most permanent gases the fully formed negative ions have mobilities greater than those of the positive ions the vapors, and in general gases or vapors having a high dielectric constant and low ionic mobility have the negative mobilities apparently equal to the positive mobilities. The question then arises do the negative ions as well as the positive ions in such gases undergo an ageing effect, or does neither ion show the change in mobility? With this end in view mobility measurements were carried out in ether vapor in which the positive ion mobility nearly equals the negative mobility as shown by Wellisch,[8] and Przibram.[9] As it would be difficult to carry out these experiments in ether with an air blast method owing to the low vapor pressure of ether at room temperatures the experiments were carried out using the Franck modification of the Rutherford method with a square wave form alternating potential from a commutator.

Applicability of Alternating Current Method.—Before proceeding to discuss the measurements on ether a short analysis of the applicability of the alternating current method to this problem and the effect of changing the auxiliary field must be made. It has been shown by the writer[10] that in the use of the gauze in the Franck modification of the alternating current method the ratio of the field below the gauze to the critical alternating potential at which the ions just cross the plates is a determining factor in the value of the mobility observed. That is, values of the mobility between 1.6 cm./sec. and 2.4 cm./sec. could be obtained for negative ions by changing this ratio through considerable limits. It was shown that this effect is due to the penetration of both fields through the gauze causing the starting point of the ions at the beginning of each phase to deviate from the assumed origin at the plane of the gauze. To a considerable extent this effect of course depends on the nature of the gauze. It is

possible that the difference in the writer's observations to be reported and Wahlin's results in air might be ascribed to this cause.

The measurements[11] were made using essentially the same type of apparatus previously described. The source of ionization was a Po coated copper disc fastened in a small cup underneath the gauze by means of wax. The gauze was a sheet of plane perforated brass having 13 circular holes of 1.5 mm. diameter per square cm. This perforated sheet 0.35 mm. thick was kept flat by being soldered to an iron ring when hot, the differential contraction on cooling keeping the gauze taut. The whole system of plates was gold plated to prevent contact differences of potential. The alternating potential came from a commutator having 30 brass segments

I. POSITIVE ION MOBILITIES AT ATMOSPHERIC PRESSURE IN AIR

PRESSURE IN MM.	AUXILIARY FIELD A	CRITICAL POTENTIAL V_0	$\frac{A}{V_0}$	POSITIVE MOBILITY REDUCED TO 760 MM.	NEGATIVE MOBILITY REDUCED TO 760 MM.
753	9.0	35	.26	1.55	....
740	4.5	40	.11	1.38	....
605	1.5	36	.042	1.25	....
605	1.5	24	.062	1.19	....
601	1.5	38	.040	....	1.81
716	4.5	54	.084	1.41	....
717	4.5	38	.12	....	2.06
252	3.0	26	.12	1.58	....
252	3.0	19	.16	....	2.09

II. POSITIVE ION MOBILITIES AT LOW PRESSURES IN AIR

PRESSURE IN MM.	AUXILIARY FIELD A	CRITICAL POTENTIAL V_0	$\frac{A}{V_0}$	POSITIVE MOBILITY REDUCED TO 760 MM.
50	7.3	62	.12	1.42
21	3.0	46	.065	1.49
20	4.5	42	.11	1.51
11	4.5	23	.20	1.52
10	1.5	9.0	.16	1.92
10	3.0	15.4	.20	1.55
9.7	1.5	14.5	.1	1.46

which could be rotated up to 2300 r.p.m. thus giving 1160 alternations per second. Several sets of spiral gears enabled the speed to be varied so that on a two segment commutator mounted on the same shaft with the 30 segment commutator as few as 15 cycles per second could be obtained. The potential applied to the commutator came from a bank of small lead storage cells of 2 ampere hours' capacity. The electrometer system had a capacity of about 300 cm. and gave a deflection of 2000 mm. per volt. The measurements in air were made on air that had slowly passed through a standard drying train of NaOH, $CaCl_2$, and two long tubes of P_2O_5. The ionic mobilities in air were measured at atmospheric pressures with different values of the auxiliary fields as a control. The mobilities of the positive

ions were also determined at pressures from 1 mm. to 5 mm. of Hg to test the Wahlin effect. The results may be summarized in the tables I and II on the preceding page.

It is evident at once that at atmospheric pressures where only completely formed normal ions were dealt with a change in the ratio of the value of the auxiliary field A to the critical potential V_0 from 0.04 to 0.16 causes changes in the mobilities of the positive and negative ion mobilities from 1.2 and 1.8 cm./sec. to 1.55 and 2.06 cm./sec., respectively. The data at more nearly constant values of A/V_0 for positive ions at low pressures show a very little deviation from the mean value of 1.5 cm./sec. Only one determination at low pressures obtained in the first series of measurements indicates the marked increase in the positive mobility at the pressures observed by Wahlin. As this could not be repeated in subsequent measurements it is doubtless due to some error. Wahlin observed changes of this magnitude (from 1.4–1.8 cm./sec.), by changing the value of the auxiliary field. The present results, which perhaps require further verification, indicate that there is with the Rutherford alternating current method little increase in the mobility of the positive ions measured in air even though the age of the ions was less than 0.003 second in the auxiliary field and 0.001 second in the measuring field.

Experiments in Ether.—The experiments in ether were made with Mallinckrodt's U. S. P. ether for Anaesthesia. The apparatus was filled by distilling the ether from a glass bulb into the ionization chamber, which had previously been pumped down to an X-ray vacuum, until the pressure was that corresponding to the vapor pressure of the ether at the room temperature. The ether was then pumped out to the requisite pressure for the measurements. The mobilities obtained reduced to 760 mm. pressure are summarized below for various values of the pressure and A/V_0, the latter being maintained as nearly constant as possible.

The tables definitely show the following facts. For nearly constant A/V_0 at 330 mm. pressure the positive ions have a lower mobility, 0.19 cm./sec., than the negative ions, 0.22 cm./sec. Although the difference is small the conditions under which the measurements were made are sufficiently similar to enable this conclusion to be drawn. At this pressure the intercepts of the current voltage mobility curves with the voltage axis were comparatively sharp. At intermediate pressures the positive ions began to increase in mobility. The increase was difficult to follow accurately due to the increase in importance of the asymptotic feet of the mobility curves occasioned by the presence of some of the faster positive ions mingled with the slower ones. At the lowest pressures the mobility curves for the positive ions again became relatively sharp and the value of the mobility of the positive ion at 5–10 mm. pressure appears quite definitely to take on the value of 0.22 cm./sec. observed for the negative ion at 330

mm. pressure. This fact has been established under nearly constant conditions of A/V_0 so that doubts cast on other results because of the effect of the auxiliary field are not applicable here. As the pressure decreases the negative ions show an increase of mobility. This increase at low pressures is definitely shown to be due to the finite time taken for the electron to attach to the ether molecule to form the negative ion. For at 40 mm. pressure the dual types of curves ascribed by Wellisch[12] and Loeb[13] to this effect appear. The ions observed in the dual curve have roughly the mobility 0.29 cm./sec. The lower intercept of the dual curve, which is due to electrons attaching in the alternating field gives an average value to the mobility of carriers attaching to form ions in the field of 2.8 cm./sec. At 10 mm. pressure the negative carriers in ether are almost exclusively free electrons it being impossible to estimate the mobility because of its high value. These measurements indicate that the electron attachment coefficient in ether is of about the same order of magnitude as that for air.

III. MOBILITIES OF POSITIVE IONS IN ETHER

PRESSURE IN MM. HG.	AUXILIARY FIELD A IN VOLTS/CM.	CRITICAL POTENTIAL V_0 IN VOLTS	$\frac{A}{V_0}$	MOBILITY OF POSITIVE IONS REDUCED TO 760 MM.
334	3.0	41	.072	.195
346	3.0	42	.071	.185
173	3.0	48	.062	.211
176	1.5	19	.079	.214
80	3.0	44.5	.068	.212
41	4.5	68.9	.066	.214
41	4.5	66.5	.068	.224
39	4.5	66.5	.068	.212
40	1.5	69.9	.022	.205
27	3.0	42	.072	.222
12.2	3.0	93.5	.032	.226
10.7	4.5	87.6	.052	.216
10.4	4.5	83.7	.055	.215
5.5	3.0	43.3	.069	.218
4.9	3.0	39.4	.075	.220

IV. MOBILITIES OF NEGATIVE IONS IN ETHER

PRESSURE IN MM. HG	AUXILIARY FIELD A IN VOLTS/CM.	CRITICAL POTENTIAL V_0 IN VOLTS	$\frac{A}{V_0}$	MOBILITY OF NEGATIVE IONS REDUCED TO 760 MM.
346	3.0	37.5	.08	.220
336	3.0	35.2	.085	.228
176	1.5	16.0	.094	.260
80.4	3.0	36.0	.083	.265
40	3.0	48.8	.062	.287*
10	All free electrons, no mobilities measureable.			

* Taken from bend in complex mobility curve.

Conclusions.—Thus the conclusion to be drawn from these experiments is that in the gases in which the mobility is small because of the high dielectric constant the mobility of the positive ion does not equal the negative mobility. There is, therefore, a difference which is however not so marked as in the more permanent gases. They further show that for newly formed ions the positive mobility has about the same value as that of the negative ions and that the mobility changes with age to the lower value found for the completely aged positive ions. The time required for this change is somewhat longer in ether than in air and is about 0.03 second. The values obtained by Yen[14] for other vapors at different pressures show the same general trend here described, although the measurements were not made with the same precautions as the present ones. His final average values are meaningless as they take the average values at different pressures, and these results show that the difference in the mobilities at different pressures is not due to accidental experimental variations but to a change in the nature of the ions with time. As these measurements were made under carefully controlled conditions and with a cognizance of the sources of error it is then probably safe to give the reduced mobilities of the gas ions in ether as 0.19 cm./sec. for the positive ions at 330 mm. and as 0.22 cm./sec. for the negative ions in ether at 330 mm. These values for the mobility constants may be assumed as holding at atmospheric pressure.

Other Positive Mobilities.—One further point might be emphasized concerning the use of the alternating current method which perhaps has been neglected. Great care must be taken in making mobility measurements that near the feet of the curves where the deflections are small and sporadic errors can occur, a sufficient number of points are taken over considerable intervals of time, to insure the elimination of these errors. If they are not eliminated the temptation becomes very great to connect them with straight lines and interpret the seeming bends or break points as due to classes of ions. This has recently been done by Wahlin[15] and Nolan[16] using the Rutherford method with an alternating potential of a sine wave form, whose steadiness cannot be absolutely relied on. In taking proper precautions the writer has not observed the curves described by the last two writers, his curves having been smooth curves approaching the voltage axis asymptotically. Where such precautions are not taken, i.e., in measurements where a set of points are taken in sequence and at about the same time during the measurement, the writer also obtained breaks which were always of the order of magnitude of the sporadic errors inherent in this type of electrometer work. On retracing this portion of the curves at a later time the irregularities cancelled out and perfectly smooth curves were obtained. Hence *one must regard with caution the results indicating that more than two positive and one negative ion of this type in gases exist.*

Theoretical Discussion.—The present experiments thus indicate that gases like ether as well as gases like air give positive ions having two mobilities, the mobility of the newly formed positive ion being equal to the single value of the mobility of the negative ion, while the other positive ion has a mobility of lower value. The measurements in He by Wahlin indicate that this takes place in He also, although a slight possibility exists that the change in mobility of the positive He ion could be ascribed to the action of impurities. Erikson[1] explains these results by assuming that the negative and newly formed positive ions are monomolecular, while the aged positive ions are bimolecular. The results in He might be interpreted as invalidating this conclusion as normally He is considered a monatomic gas. However as excited He shows a band spectrum the conclusions of Erikson may be retained. The conclusion of Erikson could be interpreted as being due to two effects of the increase in size of the ion. The increase in size of the ion might increase the mass and hence decrease the mobility, or it might also increase the radius of the ion and hence by decreasing the mean free path it would decrease the mobility. The latter view is the one taken by Erikson.

Recently the writer[17] derived an equation for the mobility of the gaseous ion based on an inverse fifth power law of force which seems to fit most of the data concerning ions quite well. This equation states that the mobility K of the ion is given by

$$K = \frac{0.104\sqrt{\frac{1+b}{b}}}{\frac{p}{760}\sqrt{(D-1)M_0}},$$

where M_0 is the molecular weight of the gas in which the ion moves, D is its dielectric constant, p is the pressure in mm. of Hg, and the factor b is the ratio of the mass of the ion to that of the molecules in which the ion moves. A somewhat similar equation was derived by Langevin[18] in 1905 on an inverse fifth power law on the basis of the rigorous kinetic theory. This equation[17] it has been shown could account for Erikson effect described above through the action of the mass factor. Recent results of Tyndall and Grindley[19] which show that the mobility of the ion is entirely independent of the mass of the ion from which it is formed (i.e., Ra B ions in air have the same mobility as air ions in air), within two per cent indicate that in this respect the theory is probably wrong. Were it not independent of the mass factor a 20% change due to the mass factor should have been observed. The theory of the writer in its present form states that the diameter of the ion has no effect on the mobility of the ions, and hence speaks against Erikson's interpretation of the effect of the diameter of the ions. As Debye, however, recently pointed out to the writer the independence of ionic

mobility and the radius of the ion lies in an assumption made by the writer in deriving the equation. This assumption is that the diameter of the molecules assumed from the kinetic theory equalled the average distance of the centers of the molecules when the two molecules were bound together by the forces of attraction between ion and molecule. This assumption while correct in order of magnitude, is not necessarily completely justified and hence it may lead to a variation of the mobility with the diameter of the molecules. Viewed in this light the theory could be brought into accord with the experimental facts. One must then conclude that these results as well as those of Tyndall and Grindley seem to demand rather important changes in the apparently otherwise satisfactory theory of the writer. It must further be concluded that until more is known about this phenomenon, the explanation given by Erikson that the change in mobility of the positive ion with time is due to a change in the diameter of the ion with increasing complexity is the most satisfactory explanation so far given.

[1] Erikson, H. A., *Physic. Rev.*, **20,** 117 (1922).
[2] Erikson, H. A., *Physic. Rev.*, **5,** 502 (1924).
[3] Erikson, H. A., *Physic. Rev.*, **6,** 622 (1924).
[4] Erikson, H. A., *Physic. Rev.*, **21,** 720 (1923).
[5] Wahlin, H. B., *Physic. Rev.*, **20,** 267 (1922).
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[11] Loeb, L. B., *J. Franklin Inst.*, **196,** 537 (1923).
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[13] Loeb, L. B., *Phys. Rev.*, **17,** 89 (1921).
[14] Yen, K. L., *Proc. Nat. Acad. Sci.*, **4,** 106 (1918).
[15] Wahlin, H. B., *Phil. Mag.*, **49,** 566 (1925).
[16] Nolan, J. J., *Phys. Rev.*, **24,** 16 (1924).
[17] Loeb, L. B., *Phil. Mag.*, **48,** 452 (1924).
[18] Langevin, P., *Ann. Chim. Phys.*, **8,** 245 (1905).
[19] Tyndall and Grindley, *Phil. Mag.*, **48,** 711 (1924).

THE PRINCIPLE OF MICROSCOPIC REVERSIBILITY

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In recent years increasing use has been made of a new postulate which perhaps cannot yet be stated in its final form, but which requires in a general way in the case of a system in thermodynamic equilibrium not only that the total number of molecules leaving a given state in unit time shall on the average equal the number arriving in that state in unit time, but also that the number leaving by any particular path shall on the average be equal to the number arriving by the reverse of that particular path, thus excluding any cyclical maintenance of the equilibrium state. The writer has ventured to name this postulate *the principle of microscopic reversibility*. The recognition that some such principle is often applicable has had a considerable history, and a brief statement as to some of the previous considerations which have come to the writer's attention will not be out of place.

As early as 1911, Kohnstamm and Scheffer[1] in considering the rates of two opposing reactions concluded that the same intermediate states occurred as steps in the reverse reactions. And in 1915, Marcelin[2] correctly concluded that the energy of the molecules in the activated states which lead to reaction has to be the same for two opposing reactions, since otherwise the temperature coefficients for the two reaction rates would not lead to the correct temperature coefficient for the equilibrium constant as given by the van't Hoff equation. Marcelin very illuminatingly likens the two opposing reactions to the migrations of people between two countries separated by a mountain range. For migration in either direction the top of the range must be crossed, in analogy with the equal energies of the activated molecules for the two opposing reactions.

A number of applications of the principle of microscopic reversibility have been made by Langmuir,[3] and as early as 1916 in connection with the problem of evaporation and condensation, he gave the following statements of the principle.

"Since evaporation and condensation are in general thermodynamically reversible phenomena, *the mechanism of evaporation must be the exact reverse of that of condensation*, even down to the smallest detail." And in a footnote "According to the principle already enunciated, by which every element in the mechanism of a reversible process must itself be reversible, it follows that any rearrangement of molecules on the surface, which takes place during the condensation of a vapor, must take place to the same extent, but in a reverse direction, in the evaporation of the substance."

Noting the words which Langmuir has italicized in the first statement, we see that by regarding this phrase as applying also to the simultaneous evaporation and condensation which are presumably taking place when the system is in equilibrium, we have a statement of the principle which agrees with the one given in the first paragraph, and as far as the writer knows this is the first explicit formulation of the principle. Furthermore, it is evident from his second statement that Langmuir appreciated the generality of the principle.

In 1917, Einstein,[4] as a necessary step in his famous deduction of the Planck radiation law, considered a molecule capable of existing in different quantum states in equilibrium with radiation, and taking a given pair of the quantum states S_m and S_n ($\epsilon_n > \epsilon_m$), equated the number of molecules passing from state S_m to state S_n by the absorption of a quantum $h\nu = \epsilon_n - \epsilon_m$ with the number passing in the reverse direction through the emission of a quantum of the same frequency. He thus used the principle of microscopic reversibility without, however, making any explicit statement of it.

In 1921, Klein and Rosseland[5] considered two reverse processes which they named collisions of the first and second kinds. In a collision of the first kind an atom is raised from a lower to a higher quantum state by using the kinetic energy of a swiftly moving electron, and in a collision of the second kind the atom drops back to the lower state giving up its energy to an electron and thus raising its velocity. By applying the principle of microscopic reversibility, Klein and Rosseland calculated the relative probability of these two kinds of collision, but again gave no explicit statement of the principle.

Several applications of the principle of microscopic reversibility especially in connection with the transfer of energy between colliding atoms have also been made by Franck,[6] and in at least two places he has made explicit statements which are closely connected with the principle. In 1923[7] he makes the statement:

"Im thermodynamischen Gleichgewicht muss jeder Elementarprozess, der in einer bestimmten Richtung n mal pro Sekunde vorkommt, einem ebensooft vorkommonenden Elementarprozess umgekehrter Richtung entsprechen." And in 1924[8] "Dieses Prinzip lautet in vereinfachter Fassung: Ein Prozess, der in einer bestimmten Richtung n mal pro Sekunde in einem gegebenen Volumen abläuft, läuft bei thermodynamischem Gleigewicht ebenfalls n mal pro Sekunde in umgekehrter Richtung ab."

It will be seen that the first of these two statements of Franck—strictly taken—seems to be merely a necessary consequence of the statistical equilibrium, since it does not definitely assert that the two opposing elementary processes which correspond to each other are the exact reverse of each other. The second statement, on the other hand, definitely equates

the number of times per second that a given elementary process proceeds in the forward and reverse direction. The impression is gained, however, that Franck has not considered the possibility of cyclical elementary processes and hence has regarded the principle as a logical necessity rather than as an independent postulate.

In 1924, it was pointed out by R. H. Fowler in connection with collisions of the first and second kind that the exclusion of cyclical elementary processes is a definite and not obviously necessary postulate, and the same thing was pointed out by the present writer for quantum transitions in general. It also seemed to the writer that the postulate was of enough interest so that it should be given a definite name, and the proposal was made that it be called "the principle of microscopic reversibility."

The statement of Fowler was made in connection with the expression of Klein and Rosseland for the relative probabilities of collisions of the first and second kinds. This expression was obtained by Klein and Rosseland with the help of the principle of microscopic reversibility, which they tacitly introduced since they stated that there would be no loss in generality in limiting their considerations to an atom which could only exist in two quantum states thus eliminating from the very start the consideration of the possibility of cyclical processes. In the case of a molecule with three quantum states, Fowler[9] makes the following remark with the reference to the possibility of making a generalization of the Klein and Rosseland result:

"But it can only be made when by an artificial limitation we have ruled out the possibility of the cyclic process $1 \longrightarrow 2$, $2 \longrightarrow 3$, $3 \longrightarrow 1$. I cannot find any convincing *a priori* reason to believe that such cycles are not permissible."

The statement of the writer[10] was as follows:

"This assumption should be recognized as a distinct postulate and might be called the principle of *microscopic* reversibility. In the case of a system in thermodynamic equilibrium, the principle would require not only that the total number of molecules leaving a given quantum state in unit time shall equal the number arriving in that state in unit time, but also the the number leaving by any one particular path shall be equal to the number arriving by the reverse of that particular path."

In 1925, Lewis[11] considered the principle of microscopic reversibility and proposed for it the name of "the law of entire equilibrium." There seems to be no reason, however, for abandoning the earlier name. Lewis stated the law in the form:

"Corresponding to every individual process there is a reverse process, and in a state of equilibrium the average rate of every process is equal to the average rate of its reverse process."

In addition to indicating some of the historical relations, the main purpose

of this note is to point out that the principle of microscopic reversibility can be regarded at the present time only as an unproved assumption. Although closely connected with the second law of thermodynamics, it cannot be derived therefrom. Lewis's attempted derivation with the help of the notion of catalytic acceleration is not convincing, since there is no reason why catalysts should not have the property of producing compensatory increases in the rates of the steps of a cyclical process. It would seem as if the postulate were a useful one, leading often at least to correct results. Nevertheless the best formulation of the principle and the precise range of its validity are matters for the future to determine.

[1] Kohnstamm and Scheffer, *Proc. Amst. Acad.*, **13,** 789 (1911). See footnote on page 795.

[2] Marcelin, *Ann. d. physique*, **3,** 173 (1915).

[3] Langmuir, *J. Amer. Chem. Soc.*, **38,** pp. 2253, 2262 (1916).

[4] Einstein, *Phys. Zts.*, **18,** 121 (1917).

[5] Klein and Rosseland, *Zts. f. Phys.*, **4,** 46 (1921).

[6] Franck, *Zts. f. Phys.*, **9,** 289 (1922); Cario and Franck, **11,** 161 (1922).

[7] Franck, "Ergebuisse der Exakten Naturwissenschaften," Zweiter Band, p. 112, Berlin, Julius Springer, 1923.

[8] Franck, "Die Naturwissenschaften, Heft 47 Zwölfter Jahrgang," p. 1066, Berlin, Julius Springer, 1924.

[9] Fowler, *Phil. Mag.*, **47,** see p. 264 (1924).

[10] Tolman, *Phys. Rev.*, **23,** see p. 699 (1924).

[11] Lewis, *Proc. Nat. Acad. Sci.*, **11,** 179 (1925).

THE DYNAMICAL FUNCTION OF THE TYMPANIC MEMBRANE AND ITS ASSOCIATED OSSICLES

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It is common knowledge to otologists and to physicists also who have been engaged in the study of deafness that lesions in the conducting mechanism of the middle ear cause a depression in the acuity of hearing for low frequency sounds only. Lesions in the internal ear with its associated nerves and nerve endings in practically all cases cause depression in hearing for the high frequency region. If the depression occurs only at high frequencies it is certain that the middle ear dynamical system functions in a normal manner. On the other hand, depressions at low frequency only, mean that the internal ear is normal.

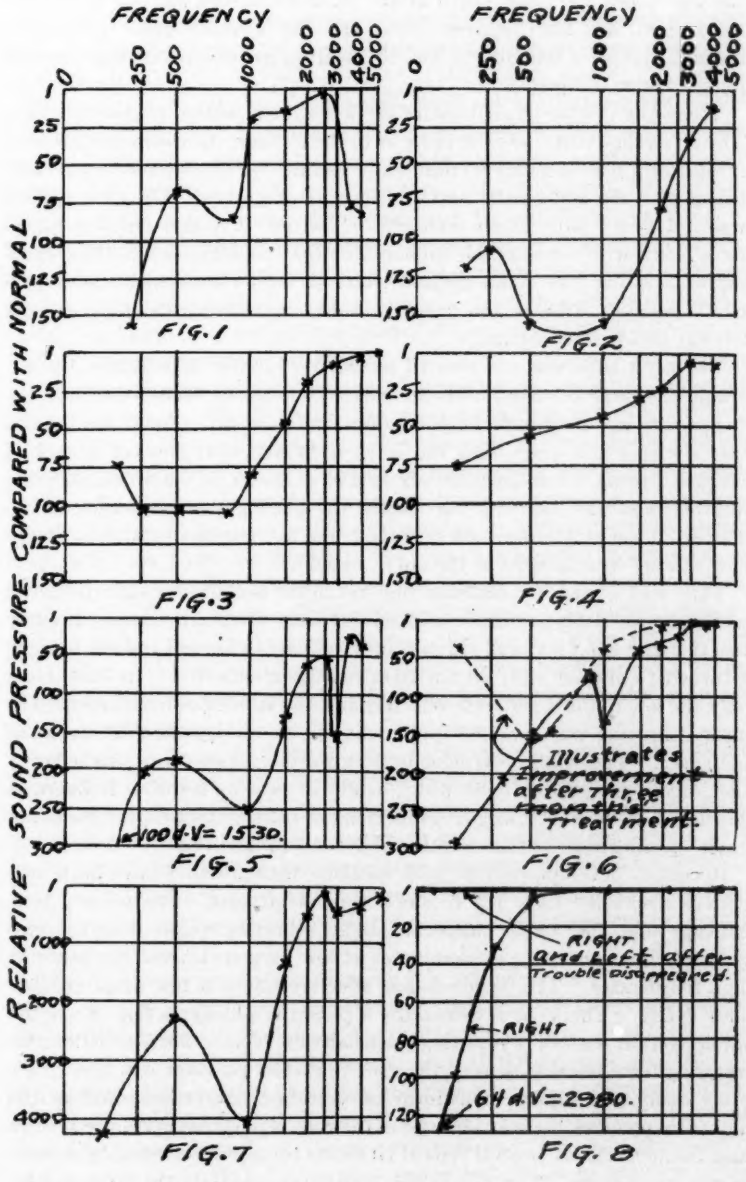
The internal ear mechanism together with its associated nerves and their endings have been intensively studied during the past five or six years by

three or four groups of physicists and otologists.[1] As a result, the function of the internal ear in the phenomena of audition is pretty well understood. The middle ear mechanism, perhaps because of its relative simplicity, has been given little consideration. The result is that some of the comparatively simple phenomena of audition have remained unexplained in a satisfactory manner. These phenomena include middle ear lesions affecting only low frequency acuity of hearing, bone conduction, increased bone conduction for middle ear lesions, greater acuity of hearing by telephone than by air, paracusis, etc. In the present contribution to this subject I believe that these phenomena are easily and quite satisfactorily explained by the theory, if it may be called such, which I propose.

A lesion in the conducting mechanism (drum and ossicle bones) acts as a barrier, so to speak, to low frequency pressure changes. The higher frequency pressure changes are transmitted without any retardation whatever. This may mean one of two things. First, the middle ear mechanism functions for low frequency sounds and some other mechanism functions for the high frequency ones. Second, the middle ear system functions in one way for the lower pitch sounds and in an entirely different manner for the higher pitch sounds. If the former case were accepted, we would be in a peculiar position for a second system does not to my knowledge exist. If we accept the second alternative, then we are called upon to show how the middle ear system can function in the two ways postulated, each independent of the other and each acting simultaneously. This I propose to do, and then try to explain all the phenomena of middle ear deafness which thus far have defied explanation in a satisfactory manner.

To illustrate the effect of this type of deafness a few curves are given herewith. In all cases with the exception of the one illustrated in Figure 7, the medical findings showed all the symptoms of middle ear lesions. In the case of Figure 7 we have illustrated the effect of congenital deafness which is frequently due to mal-development of the cochlea.

The final curves to be given are shown in Figure 8 which were taken only recently. The patient caught cold which settled first in the left eustachian tube. The effect on the ear was secondary as will be explained in a moment. The tube cleared out in a day or two and the secondary effect disappeared. Only forks were used to test the left ear during this stage. While the tube was affected the secondary effect on the ear persisted. During this stage the walls of the tubes remained closed and the blood gradually absorbed oxygen and to some extent nitrogen from the middle ear cavity, thus producing a diminished air pressure. The result of the deficiency in pressure thus created caused the drum to be pushed inward and be placed under a considerable permanent strain, the feeling of which the reader is perfectly familiar with. Fortunately this secondary effect persisted long enough to test the ear with forks. With these,


FREQUENCY
0 250 500 1000 2000 3000 4000 5000
RELATIVE SOUND PRESSURE COMPARED WITH NORMAL
1 25 50 75 100 125 150
FIG. 1
FIG. 2
FIG. 3
FIG. 4
100 d.V= 1530.
FIG. 5
Illustrates improvement after three months' treatment.
FIG. 6
1 100 200 300 400
FIG. 7
1 20 40 60 80 100 120
RIGHT and left after trouble disappeared.
RIGHT
64 d.V=2980.
FIG. 8

the low tones were not heard at all. A 384 d.v. fork was not heard; between four and five hundred cycles the ear became more and more normal, and for a tone of 512 d.v. the hearing was normal as was the case for all higher frequencies.

When the trouble cleared out of the left tube it settled in the right one. The secondary effect was the same as in the left ear, the drum being drawn inward and placed under a considerable strain. Curves for this ear were taken with the audiometer and are shown in Figure 8. The 64 d.v. tone was not heard with much certainty. The 128 d.v. and 256 d.v. tones were heard with considerable difficulty as the curve indicates. The hearing at 512 d.v. was about normal while all higher frequencies were perfectly normal. One of the curves indicates that the previously affected left ear had become normal.

The right tube was not treated medically. A few hours later, considerable discharge occurred from the nose which caused the eustachian tube to open up and permit pressure equalization to occur. The drum tension was released and tests with the forks indicated that the ear possessed normal hearing for frequencies above 256 d.v. At 128 d.v. considerable improvement was observed. At 64 d.v. the hearing was still below normal. The drum was still under some tension. Twenty-four hours later the drum and hearing were normal as the curve indicates.

This was a case of deafness due to tubal occlusion which occurred just right for study. Nature and science were certainly working prettily together and what is equally important both ears recovered and the hearing returned to normal after all our data had been collected. In both cases only the low frequencies were affected and the transition from impaired to normal hearing was confined quite definitely to the region of 500 cycles in both ears. The strain or tension in the inwardly drawn drum affected only that mode of vibration upon which acuity of hearing for low frequencies depended without affecting or influencing to the slightest degree the other mode of vibration used for audition above 500 cycles or so.

Recently, developments in loud speakers with which I have been intimately associated have led to a new type of speaker. Preliminary tests indicate that the freely supported, light, vibrating, paper cone has two types of vibrations—one predominates at low frequencies and the other at high frequencies. The former is less effective above a few hundred (say 500) cycles. This type is essentially a piston or plunger action, where the whole conical surface is vibrating essentially in phase. There is little or no restoring force tending to keep the cone in its rest-position, it is free to vibrate easily as a whole. This form of vibration exerts less effect at the higher frequencies, because the mass of the cone is too great to vibrate at these high frequencies. A flexural type of vibration becomes predominate at these higher frequencies. The two types of vibration overlap, the latter begin-

ning at about 250 cycles (depending on the size of the cone) and the former ending at perhaps 600 or 700 cycles. Above this, flexural vibrations greatly predominated and below 300 cycles or so the piston type exert practically the whole effect.

This reference to the loud speaker is sufficient to illustrate the vibrational characteristics which the ear drum and ossicle bones possess. At low frequencies the drum, being very freely supported to the bony wall at its periphery, is free to vibrate as a piston. The multiplying lever action of ossicle bones and the ratio of the drum area to that of the oval window (20 to 1) combine to permit relatively large pressure changes to act on the oval window and be transmitted by the liquid of the labyrinth to the anterior portion of the basilar membrane where the low frequency nerve endings are located. Nature has beautifully endowed the middle ear to perform just this function in audition.

The transition to the flexural type of vibration occurs in the region of 400 to 500 cycles. At the latter frequency the piston action has ceased to be a factor of much importance. For this type of vibration the ossicles probably fail to function as a system of multiplying levers, but serve to conduct the flexural vibrational energy of the drum by means of longitudinal or molecular vibrations to the oval window. Perhaps for these higher frequencies the pressure-increase at the lower pitches due to the ratio of area of the drum to that of the oval window has no effect. In a true sense, then, the ossicle bones are a *conducting* mechanism for the higher frequencies. For the lower frequencies, however, they are a lever or multiplying mechanism. Let us, then, apply the results of the present discussion to explain some of the phenomena of middle ear lesions as given above and as known to otologists.

For these explanations it is not necessary to go into them in detail as the application of the theory to various cases is direct enough. Any constraint in the ossicle bones, increased tension in the drum, displacement of the bones or drum will introduce constraints in the middle ear system as a whole and its freedom of motion will be reduced. Hearing for low frequencies will be reduced in direct proportion to the magnitude of the constraints for it will become increasingly difficult for the system to vibrate freely as a piston.

High frequency perception may and in many cases will be affected. From the nature of things, the flexural vibrations of the drum will be affected to a more or less extent by middle ear lesions. However, these vibrations can continue little impeded even if the drum is affected. It is a matter of record that the drum and ossicles may be wanting entirely and hearing not be far below normal for the higher frequencies but considerably below normal for the low frequencies. This has been amply proven experimentally. I have also demonstrated this in the case of the

freely supported, paper cone type of loud speaker. Constraints applied to the paper cone to stop the piston action did so without influencing to any noticeable extent the high frequencies produced by flexural vibrations—the amplitude of the former being perhaps 500 to 1000 times greater than that of the latter at their extreme ranges for equal sound radiation. These two types of motion are possible because the cone is quite stiff structurally but offers little rigidity to flexural vibrations, the velocity of these vibrations being only about 20 meters per second. No doubt the conical shape of the tympanic membrane is of vital importance for these characteristics as in the case of the conical loud speakers.

Otologists use what is known as the Weber test. It is a bone conduction test and is made by holding the tuning fork on the top of the head to observe in which ear the sound is best heard. It always seems to be heard in the ear in which a lesion of the middle ear is located. If both ears are normal, the sound is heard equally well in both ears. The test applies only to the lower frequency forks for the head is too massive to be vibrated by the higher pitch forks. This would indicate that normal bone conduction, perhaps to a large extent, is brought about by vibration of the cranial bones as a whole.

The application of the theory to this phenomenon is simple enough. Under normal conditions the drum and ossicles are too freely supported to be considered part of the bony walls of the ear. In normal bone conduction, then, these parts of the ear do not greatly influence the process. When, however, a middle ear lesion puts a constraint in the drum and ossicles these become more intimately connected to the bony walls of the ear and increased bone conduction results. Therefore, when this occurs an additional amount of sound pressure can now be transmitted directly to the inner ear through the drum, ossicle bones and the footplate of the stapes. Under this condition the pressure is applied in a normal way and is thus most effective. The difference, of course, will be greatly noticeable only at the low frequencies and vanish at the high frequencies for the reason of the massiveness of the head as noted above.

Another observation, due to the otologists, is that with middle ear deafness a patient can hear better over the telephone than directly through the air. This is explainable rather simply, because increased bone conduction from the telephone receiver case can to some extent make up for the loss in hearing at the low frequencies. High frequencies are not lost and bone conduction at high frequencies is not present and, hence, high frequencies do not require any adjustment.

Finally we come to what otologists call paracusis. They maintain that persons having certain types of middle ear lesions hear better in the presence of rather intense noises than in the quiet places. This is partly explained by the statement that in noisy places people talk louder than in

quiet places. This is true, but I hardly think that the relative intensity of the voice sounds and the noise is such as to enable the person afflicted with middle ear deafness to hear better because of the increased voice energy. Perhaps there are two factors involved which now can be better understood. In the first place when people talk louder than usual, their voices become high pitched and the overtones become much more prominent. In the second place the acuity of hearing for these higher pitch sounds is greater than for those of lower pitch. Through long experience with deaf people I always try to make them understand first by raising the pitch of my voice and at the same time talking louder. I am thus able to excite more of the flexural type of vibration of the drum and less of the piston type for which we are considering that there is a considerable restraining action. Probably the louder talking has less effect than the increased pitch, because usually women's voices are more easily understood than men's by people afflicted with middle ear deafness. The reason, I think, is because of differences pointed out in this discussion. In any case, the effect we are discussing is probably not large.

Another explanation of paracusis advanced by some writers is that loud noises cause the drum and ossicles to vibrate with more intensity and under this condition they become freer and can then become more sensitive for speech sounds. I think probably this is hardly the case for even more or less normal ears would observe the effect. On the whole, I should feel inclined to give greater weight to the explanation advanced in the preceding paragraph, particularly in view of the fact that it has as its basis experimental observations which seem to fit in satisfactorily with the theory which I have advanced.

[1] (*a*) Seashore, Dr. Dean and Bunch, Iowa City, Iowa; (*b*) Sabine and Kranz, Geneva, Ill.; (*c*) Dr. Fowler, Fletcher and Wegel, New York City; (*d*) Dr. Wilson and Minton, Chicago, Ill.; (*e*) Dr. Rae and Minton, New York City.

A NEW CRYSTAL FOR WAVE-LENGTH MEASUREMENTS OF SOFT X-RAYS

BY LINUS PAULING AND ALBERT BJÖRKESON

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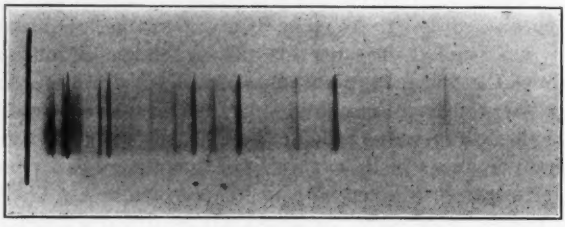
During an investigation of the crystal structures of hematite and corundum[1] spectral photographs of the K-radiation of molybdenum reflected from the plane (00.1) of the hexagonal crystal β-alumina,[2] Al_2O_3, were made. One such photograph is shown in the accompanying reproduction.

Upon substituting in the equation $n\lambda = 2d \sin \theta$ the wave-lengths λ of the X-rays used and the corresponding angles of reflection θ, the grating-constant d was found to be about 11.2 Å, assuming that n is unity for the reflection at the smallest angle. This result shows that this substance has an unusually large grating-constant; and, since this is accompanied by strong reflection, the crystal should prove of great value in the measurement of wave-lengths of soft X-rays.



In order to determine accurately the value of the grating-constant, photographs were taken of the lines $L\alpha_1$ of silver (first order) and $K\alpha_1$ of copper (second order), using a vacuum spectrograph similar to that of Siegbahn,[3] and using his double exposure method.[4] As source for the X-radiation hot sparks[5] were used. The following data were obtained:

LINE	WAVE-LENGTH	ORDER OF REFLECTION	ANGLE OF REFLECTION	GRATING-CONSTANT
Cu $K\alpha_1$	1.53730 Å	2	7° 51′ 41″	11.240 Å
Ag $L\alpha_1$	4.14564 Å	1	10° 38′ 29″	11.225 Å

Several photographs were taken, and the values of d calculated from them varied by less than 0.002 Å from the averaged values given above. The dependence of the grating-constant on the angle of reflection seems to be a real effect. This involves deviation from the Bragg equation, but is in agreement with previous investigations.[6]

The following relative intensities of reflection in successive orders were observed: first and second, very strong; third, weak; fourth and fifth, strong; sixth, very weak; seventh, medium strong; eighth, very weak; ninth, medium weak; tenth, medium.

The crystals previously used with soft X-rays have smaller grating-constants than this crystal; that for (100) of sucrose being 10.57 Å and for the cleavage face of mica 10.1 Å. Moreover, these crystals are soft, and the reflections they give in small orders are not strong. These disadvantages do not exist in the case of β-alumina. The crystals of β-alumina are in the form of basal plates, some of which are of perfect internal structure and give very sharp reflections. They can be obtained with faces large enough for use in spectrographic work; the specimen[7] used in obtaining the values reported in this note possessed a good face about 1 cm.

square. The hardness of the crystal is equal to that of corundum (9 on Mohs' scale), so that specimens are not easily scratched or deformed. The theoretical maximum wave-length of X-rays with which the crystal can be used is $2d$, or about 22.5 Å, corresponding to an angle of reflection of 90°; the wave-length corresponding to an angle of reflection of 60° is about 19.5 Å.

Previous attempts to find crystals with large grating-constants have been restricted to substances with complicated chemical formulas; such a procedure appears unnecessary in light of the surprising discovery of the unusually large constant possessed by crystals of the simple inorganic substance β-alumina.

[1] Linus Pauling and S. B. Hendricks, *J. Amer. Chem. Soc.*, **47**, 781 (1925).

[2] G. A. Rankine and H. E. Merwin, *J. Amer. Chem. Soc.*, **38**, 568 (1916).

[3] M. Siegbahn, "Spektroskopie der Röntgenstrahlen," Julius Springer, Berlin, 1924, p. 70.

[4] Ref. 3, p. 60.

[5] Albert Björkeson, *Proc. Nat. Acad.* This number, p. 413.

[6] Ref. 3, p. 24.

[7] We wish to thank Dr. A. A. Klein of the Norton Company, Worcester, Mass., for this speciman; also Dr. R. G. Dickinson of this Institute, and Dr. R. W. G. Wyckoff of the Geophysical Laboratory, for supplying us with some crystals, from the same source, used in our preliminary work.

ON QUASI-ANALYTIC FUNCTIONS

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A recent note of G. Julia in the *Comptes Rendes de l'Academie des Sciences in Paris* (**180,** p. 720, March, 1925) may have most remarkable consequences in the coming years, as appears if we pay attention to the general properties of quasi-analytic functions and their mutual relations.

As yet, calculations and special studies in Calculus have, above all, concerned analytic functions. Where does this quite special importance come from? It is clear that it is due to two main circumstances, which are:

(1) That the simplest known functions—beginning with $y=f(x)=x$ itself—those which we want it the most elementary and usual calculations, are analytic:

(2) That they generate each other by the main operations of Calculus: algebraic operation, substitution of functions in functions, differentiation, integration, and so on—i.e., carrying out such operations on analytic functions always leads to functions which are again analytic.

Quasi-analytic functions, or, more exactly, definite classes of quasi-analytic functions, also admit of the latter property. Therefore, if amongst

them, there would arise any special one which would prove of importance, the consequence would be that the whole corresponding class would play its role in analysis in a manner analogous to usual analytic functions.

Now, this is precisely what Julia's note shows to be quite possible: for he finds that certain classes of quasi-analytic functions are necessarily to be introduced in the study of some problems concerning iterations.

If it should happen that any special series constituted with iterated functions appears in a concrete problem and, therefore, became an object of calculations, we should have that paradoxial consequence that, in some researches certain classes of quasi-analytic functions would become as usual and important as analytic ones.

SUR LE CALCUL APPROCHÉ DES INTEGRALES DEFINIES

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La méthode la plus simple et celle qui se présente la première a l'esprit pour l'évaluation approchée de l'intégrale définie $\int_a^b f(x)dx$—celle des trapèzes—a été améliorée dans plusieurs sens. La méthode de *Simpson* consiste, comme on sait, à prendre pour le nombre des divisions, supposées égales entre elles, une valeur paire $2n$, ces intervalles étant groupés deux par deux et, dans chaque couple d'intervalles ainsi constitués, à remplacer la fonction f par un polynôme d'interpolation du second degré prenant les mêmes valeurs aux trois points (extrêmes et médian) de division. Si, pour commencer, nous nous bornons à un seul couple d'intervalles, de longueur l chacun, l'origine des abscisses étant prise au point médian, la methode conduit, pour l'intégrale partielle correspondante

$$i = \int_{-l}^{+l} f(x)dx$$

à la valeur approchée

$$j_1 = \frac{l}{3}\Big[f(l) + f(-l) + 4f(o)\Big], \tag{1}$$

l'intégrale totale

$$I = \int_a^b f(x)dx$$

étant, en conséquence remplacée par l'expression

$$J_1 = \frac{b-a}{3n}(A + 2B) \tag{2}$$

où A et B sont respectivement la somme des ordonnées de rang pair (les deux extrêmes étant comptées pour noitié) et la somme des ordon nées de rang impair

$$A = \frac{1}{2}f(a) + \sum_{q=1}^{n-1} f\left(a + q\,\frac{b-a}{n}\right) + \frac{1}{2}f(b),$$
$$B = \sum_{q=1}^{n} f\left[\left(q - \frac{1}{2}\right)\frac{b-a}{n}\right]. \qquad (3)$$

La méthode d'*Euler Maclaurin* prend, au contraire, comme point de départ le résultat même fourni par la méthode des trapèzes, savoir (1), et l'améliore par une série de termes correctifs dont nous ne retidendrons d'ailleurs que le premier, égal, comme on le sait, à $-\frac{l^2}{12}[f'(b)-f'(a)] = -\frac{(b-a)^2}{12m^2}[f'(b)-f'(a)]$, en désignant par m le nombre des parties (égales entre elles) en lesquelles on divise l'intervalle d'intégration (a, b) et par l leur granleur commune.

Pour comparer entre elles ces deux méthodes, il convient évidemment de prendre $m = 2n$. Le résultat obtenu par la première correction d'Euler Maclaurin sera, dans ces conditions,

$$\frac{b-a}{2n}(A+B) - \frac{l^2}{12}[f'(b) - f'(a)],$$

A et B désignant encore les quantités (3). Pour le couple unique d'intervalles $(-l, 0, +l)$, c'est à dire, pour le cas de $m = 2$, il vient l'expression

$$j_2 = \frac{l}{2}[f(l) + f(-l) + 2f(o)] - \frac{l^2}{12}[f'(l) - f'(-l)].$$

Nous comparerons les deux modes de calcul que nous venons de mentionner en supposant l infiniment petit et $f(x)$ développée en série entière

$$f(x) = C_0 + C_1 x + \ldots + C_p x^p + \ldots$$

On trouve sans difficulté, dans ces conditions, que la différence $i-j_1$ commence par les termes

$$-4/15\ C_4 l^5 - 8/21\ C_6 l^7 \ldots \qquad (4)$$

et la différence $i-j_2$ par les termes

$$1/15\ C_4 l^5 + 2/7\ C_6 l^7 \ldots \qquad (5)$$

On voit donc que l'erreur commise après correction de la méthode des trapèzes par le premier terme d'Euler Maclaurin est de signe contraire à celle que donne la méthode Simpson et sensiblement quatre fois plus petite.

Mais il ressort de là une autre conséquence plus importante: la combinai-

son des deux expressions précédentes nour fournit, sans calcul nouveau, une approximation notablement meilleure que les deux précédentes. Nous voyone, en effet, que la quantité

$$j = 1/5\, j_1 + 4/5\, j_2$$

a en commun avec l'intégrale cherchée non seulement les termes d'ordre 3, mais les termes d'ordre 5, ceux-ci d'éliminant, dans une telle combinaison, entre les expressions (4) et (5). La différence $i-j$ commence par le terme

$$\frac{16}{105} C_6 l^7 = \frac{16}{3.5.7} C_6 l^7 = \frac{f^{(6)}(o)}{3^2.5^2.7} l^7, \tag{6}$$

qui, dans notre evaluation actuelle, peut encore se remplacer par

$$\frac{l^6}{2.3^2.5^2.7} [f^{(5)}(l) - f^{(5)}(-l)]. \tag{6 bis}$$

Il y aura onc un avantage évident à opérer ainsi sur chacun des $2n$ intervalles partiels en lesquels (a, b) est divisé et à prendre pour I la valeur approchée

$$J = 1/5\, J_1 + 4/5\, J_2,$$

soit, en introduisant les sommes A et B,

$$J = \frac{b-a}{15n}(7A + 8B) - \frac{(b-a)^2}{60n^2}[f'(b) - f'(a)]. \tag{7}$$

Si les divisions de notre intervalle sont assez petites pour que les évaluations précédentes soient légitimes dans chacune d'elles, les termes d'ordre supé rieur étant négligeables, l'erreur commise en adoptant cette dernière valeur approchée sera sensiblement de la forme $\frac{1}{3^2.5^2.7}\left(\frac{b-a}{2n}\right)^7 \sum_{q=1}^{n} \left[f^{(6)}\left(\frac{2_{q-1}}{2}\frac{b-a}{n}\right)\right]$, quantité inférieure à $\frac{n}{3^2.5^2.7}\left(\frac{b-a}{2n}\right)^7 M_6$, en désignant par M_6 un maximum du module de la dérivée sixieme; ou si l'ou veut, en utilisant (6 *bis*) au lieu de (6),

$$\frac{1}{2.3^2.5^2.7}\left(\frac{b-a}{2n}\right)^6 [f^{(5)}(b) - f^{(5)}(a)].$$

Cette nouvelle expression J parait donc offrir au point de vue du calcul un avantage sérieux, puisqu'elle fournit une meilleure approximation que J_2 sans exi ger le calcul d'aucun élément nouveau.

On pourrait généraliser la remarque précédente, et en tirer l'appliquer à des améliorations analogues pour des valeurs approchées d'ordre plus élevé. M. Andoyer, que j'ai entretenu de cette question, a bien voulu me faire part de réflexions importantes dans ce sens.